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(54) Title: FUNCTIONALIZED FIBRILS

(57) Abstract

Graphitic nanotubes, which includes tubular fullerenes (commonly called "buckytubes") and fibrils, which are functionalized by chemical substitution or by adsorption of functional moieties. More specifically the invention relates to graphitic nanotubes which are uniformly or non-uniformly substituted with chemical moieties or upon which certain cyclic compounds are adsorbed and to complex structures comprised of such functionalized fibrils linked to one another. The invention also relates to methods of introducing functional groups onto the surface of such fibrils.

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FUNCTIONALIZED FIBRILS

FIELD OF THE INVENTION

The invention relates broadly to graphitic nanotubes, which includes tubular fullerenes (commonly 5 called "buckytubes") and fibrils, which are functionalized by chemical substitution or by adsorption of functional moieties. More specifically the invention relates to graphitic nanotubes which are uniformly or non-uniformly substituted with chemical moieties or upon 10 which certain cyclic compounds are adsorbed and to complex structures comprised of such functionalized fibrils linked to one another. The invention also relates to methods of introducing functional groups onto the surface of such fibrils.

15

BACKGROUND OF THE INVENTION

This invention lies in the field of submicron graphitic fibrils, sometimes called vapor grown carbon fibers. Carbon fibrils are vermicular carbon deposits having diameters less than 1.0μ , preferably less than 20 0.5μ , and even more preferably less than 0.2μ . They exist in a variety of forms and have been prepared through the catalytic decomposition of various carbon-containing gases at metal surfaces. Such vermicular carbon deposits have been observed almost since the 25 advent of electron microscopy. A good early survey and reference is found in Baker and Harris, Chemistry and Physics of Carbon, Walker and Thrower ed., Vol. 14, 1978, p. 83, hereby incorporated by reference. See also, Rodriguez, N., J. Mater. Research, Vol. 8, p. 3233 30 (1993), hereby incorporated by reference.

In 1976, Endo et al. (see Obelin, A. and Endo, M., J. of Crystal Growth, Vol. 32 (1976), pp. 335-349, hereby incorporated by reference) elucidated the basic mechanism by which such carbon fibrils grow. There were 35 seen to originate from a metal catalyst particle, which, in the presence of a hydrocarbon containing gas, becomes supersaturated in carbon. A cylindrical ordered

graphitic core is extruded which immediately, according to Endo et al., becomes coated with an outer layer of pyrolytically deposited graphite. These fibrils with a pyrolytic overcoat typically have diameters in excess of 5 0.1μ , more typically 0.2 to 0.5μ .

In 1983, Tennent, U.S. Patent No. 4,663,230, hereby incorporated by reference, succeeded in growing cylindrical ordered graphite cores, uncontaminated with pyrolytic carbon. Thus, the Tennent invention provided 10 access to smaller diameter fibrils, typically 35 to 700 Å (0.0035 to 0.070μ) and to an ordered, "as grown" graphitic surface. Fibrillar carbons of less perfect structure, but also without a pyrolytic carbon outer layer have also been grown.

15 The fibrils, buckytubes and nanofibers that are functionalized in this application are distinguishable from continuous carbon fibers commercially available as reinforcement materials. In contrast to fibrils, which have, desirably large, but unavoidably finite aspect 20 ratios, continuous carbon fibers have aspect ratios (L/D) of at least 10^4 and often 10^6 or more. The diameter of continuous fibers is also far larger than that of fibrils, being always $>1.0\mu$ and typically 5 to 7μ .

Continuous carbon fibers are made by the 25 pyrolysis of organic precursor fibers, usually rayon, polyacrylonitrile (PAN) and pitch. Thus, they may include heteroatoms within their structure. The graphitic nature of "as made" continuous carbon fibers varies, but they may be subjected to a subsequent 30 graphitization step. Differences in degree of graphitization, orientation and crystallinity of graphite planes, if they are present, the potential presence of heteroatoms and even the absolute difference in substrate diameter make experience with continuous fibers poor 35 predictors of nanofiber chemistry.

Tennent, U.S. Patent No. 4,663,230 describes carbon fibrils that are free of a continuous thermal

carbon overcoat and have multiple graphitic outer layers that are substantially parallel to the fibril axis. As such they may be characterized as having their c-axes, the axes which are perpendicular to the tangents of the curved layers of graphite, substantially perpendicular to their cylindrical axes. They generally have diameters no greater than 0.1μ and length to diameter ratios of at least 5. Desirably they are substantially free of a continuous thermal carbon overcoat, i.e., pyrolytically deposited carbon resulting from thermal cracking of the gas feed used to prepare them.

Tennent, et al., US Patent No. 5,171,560, hereby incorporated by reference, describes carbon fibrils free of thermal overcoat and having graphitic layers substantially parallel to the fibril axes such that the projection of said layers on said fibril axes extends for a distance of at least two fibril diameters. Typically, such fibrils are substantially cylindrical, graphitic nanotubes of substantially constant diameter and comprise cylindrical graphitic sheets whose c-axes are substantially perpendicular to their cylindrical axis. They are substantially free of pyrolytically deposited carbon, have a diameter less than 0.1μ and a length to diameter ratio of greater than 5. These fibrils are of primary interest in the invention.

Further details regarding the formation of carbon fibril aggregates may be found in the disclosure of Snyder et al., U.S. Patent Application Serial No. 149,573, filed January 28, 1988, and PCT Application No. 30 US89/00322, filed January 28, 1989 ("Carbon Fibrils") WO 89/07163, and Moy et al., U.S. Patent Application Serial No. 413,837 filed September 28, 1989 and PCT Application No. US90/05498, filed September 27, 1990 ("Fibril Aggregates and Method of Making Same") WO 91/05089, all 35 of which are assigned to the same assignee as the invention here and are hereby incorporated by reference.

Moy et al., USSN 07/887,307 filed May 22, 1992, hereby incorporated by reference, describes fibrils prepared as aggregates having various macroscopic morphologies (as determined by scanning electron microscopy) in which they are randomly entangled with each other to form entangled balls of fibrils resembling bird nests ("BN"); or as aggregates consisting of bundles of straight to slightly bent or kinked carbon fibrils having substantially the same relative orientation, and having the appearance of combed yarn ("CY") e.g., the longitudinal axis of each fibril (despite individual bends or kinks) extends in the same direction as that of the surrounding fibrils in the bundles; or, as, aggregates consisting of straight to slightly bent or kinked fibrils which are loosely entangled with each other to form an "open net" ("ON") structure. In open net structures the degree of fibril entanglement is greater than observed in the combed yarn aggregates (in which the individual fibrils have substantially the same relative orientation) but less than that of bird nests. CY and ON aggregates are more readily dispersed than BN making them useful in composite fabrication where uniform properties throughout the structure are desired.

When the projection of the graphitic layers on the fibril axis extends for a distance of less than two fibril diameters, the carbon planes of the graphitic nanofiber, in cross section, take on a herring bone appearance. These are termed fishbone fibrils. Geus, U.S. Patent No. 4,855,091, hereby incorporated by reference, provides a procedure for preparation of fishbone fibrils substantially free of a pyrolytic overcoat. These fibrils are also useful in the practice of the invention.

Carbon nanotubes of a morphology similar to the catalytically grown fibrils described above have been grown in a high temperature carbon arc (Iijima, *Nature* 354 56 1991). It is now generally accepted (Weaver,

Science 265 1994) that these arc-grown nanofibers have the same morphology as the earlier catalytically grown fibrils of Tennent. Arc grown carbon nanofibers are also useful in the invention.

5 McCarthy et al., U.S. Patent Application Serial No. 351,967 filed May 15, 1989, hereby incorporated by reference, describes processes for oxidizing the surface of carbon fibrils that include contacting the fibrils with an oxidizing agent that includes sulfuric acid 10 (H_2SO_4) and potassium chlorate ($KClO_3$) under reaction conditions (e.g., time, temperature, and pressure) sufficient to oxidize the surface of the fibril. The fibrils oxidized according to the processes of McCarthy, et al. are non-uniformly oxidized, that is, the carbon 15 atoms are substituted with a mixture of carboxyl, aldehyde, ketone, phenolic and other carbonyl groups.

Fibrils have also been oxidized non-uniformly by treatment with nitric acid. International Application PCT/US94/10168 discloses the formation of oxidized 20 fibrils containing a mixture of functional groups.

Hoogenvaad, M.S., et al. ("Metal Catalysts supported on a Novel Carbon Support", Presented at Sixth International Conference on Scientific Basis for the Preparation of Heterogeneous Catalysts, Brussels, Belgium, September 25 1994) also found it beneficial in the preparation of fibril-supported precious metals to first oxidize the fibril surface with nitric acid. Such pretreatment with acid is a standard step in the preparation of carbon-supported noble metal catalysts, where, given the usual 30 sources of such carbon, it serves as much to clean the surface of undesirable materials as to functionalize it.

In published work, McCarthy and Bening (Polymer Preprints ACS Div. of Polymer Chem. 30 (1) 420 (1990)) prepared derivatives of oxidized fibrils in order to 35 demonstrate that the surface comprised a variety of oxidized groups. The compounds they prepared, phenylhydrazones, haloaromatic esters, thallous salts,

etc., were selected because of their analytical utility, being, for example, brightly colored, or exhibiting some other strong and easily identified and differentiated signal. These compounds were not isolated and are, 5 unlike the derivatives described herein, of no practical significance.

While many uses have been found for carbon fibrils and aggregates of carbon fibrils, as described in the patents and patent applications referred to above, 10 many different and important uses may be developed if the fibril surfaces are functionalized. Functionalization, either uniformly or non-uniformly, permits interaction of the functionalized fibrils with various substrates to form unique compositions of matter with unique properties 15 and permits fibril structures to be created based on linkages between the functional sites on the fibrils' surfaces.

OBJECTS OF THE INVENTION

It is therefore a primary object of this 20 invention to provide functionalized fibrils, i.e. fibrils whose surfaces are uniformly or non-uniformly modified so as to have a functional chemical moiety associated therewith.

It is a further and related object of this 25 invention to provide fibrils whose surfaces are functionalized by reaction with oxidizing or other chemical media.

It is a further and related object of this invention to provide fibrils whose surfaces are uniformly 30 modified either by chemical reaction or by physical absorption of species which themselves have a chemical reactivity.

It is a further object to provide fibrils whose surfaces have been modified e.g. by oxidation which are 35 then further modified by reaction with functional groups.

It is still a further and related object of this invention to provide fibrils whose surfaces are

modified with a spectrum of functional groups so that the fibrils can be chemically reacted or physically bonded to chemical groups in a variety of substrates.

It is still the further and related object of 5 this invention to provide complex structures of fibrils by linking functional groups on the fibrils with one another by a range of linker chemistries.

It is still a further and related object of 10 this invention to provide methods for chemical modification of fibril surfaces and methods for physically absorbing species on the surfaces of fibrils so as to provide, in each case, a functional moiety associated with the surface of the fibril.

It is yet a further object of this invention to 15 provide new compositions of matter based upon the functionalized fibrils.

DETAILED DESCRIPTION OF THE INVENTION

These and other objects of the invention are achieved in compositions which broadly have the formula

20 $[C_nH_L]^mR_m$

where n is an integer, L is a number less than 0.1n, m is a number less than 0.5n,

each of R is the same and is selected from 25 SO_3H , $COOH$, NH_2 , OH , CHO , CN , $COCl$, halide, $COSH$, SH , $COOR'$, SR' , SiR'_3 , $Si(O-OR')_yR'^{3-y}$, $Si(O-SiR'_2)OR'$, R'' , Li , AlR'_2 , $Hg-X$, TlZ_2 and $Mg-X$,

y is an integer equal to or less than 3,

R' is alkyl, aryl, cycloalkyl or aralkyl,

R'' is fluoroalkyl, fluoroaryl,

30 fluorocycloalkyl, fluoroaralkyl or cycloaryl,

X is halide, and

Z is carboxylate or trifluoroacetate.

The carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic nanotube of 35 substantially constant diameter. The nanotubes include those having a length to diameter ratio of greater than 5 and a diameter of less than 0.5μ , preferably less than

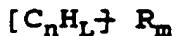
0.1 μ . The nanotubes can also be substantially cylindrical, graphitic nanotubes which are substantially free of pyrolytically deposited carbon, more preferably those characterized by having a projection of the 5 graphite layers on the fibril axis which extends for a distance of at least two fibril diameters and/or those having cylindrical graphitic sheets whose c-axes are substantially perpendicular to their cylindrical axis. These compositions are uniform in that each of R is the 10 same.

Non-uniformly substituted nanotubes are also prepared. These include compositions of the formula



where n, L, m, R and the nanotube itself are as defined 15 above, provided that each of R does not contain oxygen, or, if each of R is an oxygen-containing group COOH is not present.

Functionalized nanotubes having the formula



20 where n, L, m, R and R' have the same meaning as above and the carbon atoms are surface carbon atoms of a fishbone fibril having a length to diameter ratio greater than 5, are also included within the invention. These may be uniformly or non-uniformly substituted.
25 Preferably, the nanotubes are free of thermal overcoat and have diameters less than 0.5 μ .

Also included in the invention are functionalized nanotubes having the formula



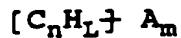
30 where n, L, m, R' and R have the same meaning as above. The carbon atoms, C_n, are surface carbons of a substantially cylindrical, graphitic nanotube of substantially constant diameter. The nanotubes have a length to diameter ratio of greater than 5 and a diameter 35 of less than 0.5 μ , preferably less than 0.1 μ . The nanotubes may be nanotubes which are substantially free of pyrolytically deposited carbon. More preferably, the

nanotubes are those in which the projection of the graphite layers on the fibril axes extends for a distance of at least two fibril diameters and/or those having cylindrical graphitic sheets whose c-axes are 5 substantially perpendicular to their cylindrical axis.

In both uniformly and non-uniformly substituted nanotubes, the surface atoms C_n are reacted. Most carbon atoms in the surface layer of a graphitic fibril, as in graphite, are basal plane carbons. Basal plane carbons 10 are relatively inert to chemical attack. At defect sites, where, for example, the graphitic plane fails to extend fully around the fibril, there are carbon atoms analogous to the edge carbon atoms of a graphite plane (See Urry, *Elementary Equilibrium Chemistry of Carbon*, 15 Wiley, New York 1989.) for a discussion of edge and basal plane carbons).

At defect sites, edge or basal plane carbons of lower, interior layers of the nanotube may be exposed. The term surface carbon includes all the carbons, basal 20 plane and edge, of the outermost layer of the nanotube, as well as carbons, both basal plane and/or edge, of lower layers that may be exposed at defect sites of the outermost layer. The edge carbons are reactive and must contain some heteroatom or group to satisfy carbon 25 valency.

The substituted nanotubes described above may advantageously be further functionalized. Such compositions include compositions of the formula



30 where the carbons are surface carbons of a nanotube, n, L and m are as described above,

A is selected from

35
$$\begin{array}{cccc} O & O & O & O \\ || & || & || & || \\ OY, & NHY, & C-OY, & C-NR'Y, & C-SY, & C-Y, & -CR'_2-OY, & N=Y \text{ or} \\ & & & & & & & C=Y, \end{array}$$

Y is an appropriate functional group of a protein, a peptide, an enzyme, an antibody, a nucleotide,

an oligonucleotide, an antigen, or an enzyme substrate, enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from R'-OH, R'-NH₂, R'SH, R'CHO, R'CN, R'X, R'SiR'₃, R'Si(OR')_yR'_{3-y}, R'Si(OR')₂R', R'-R", R'-N-CO, (C₂H₄O)_wH, (C₃H₆O)_wH, (C₂H₄O)_wR', (C₃H₆O)_w-R' and R', and

5 w is an integer greater than one and less than 200.

10 The carbon atoms, C_n, are surface carbons of a substantially cylindrical, graphitic nanotube of substantially constant diameter. The nanotubes include those having a length to diameter ratio of greater than 5 and a diameter of less than 0.1μ, preferably less than 0.05μ. The nanotubes can also be substantially cylindrical, graphitic nanotubes which are substantially free of pyrolytically deposited carbon. More preferably they are characterized by having a projection of the graphite layers on the fibril axes which extends for a distance of at least two fibril diameters and/or they are

15 20 comprised of cylindrical graphitic sheets whose c-axes are substantially perpendicular to their cylindrical axes. Preferably, the nanotubes are free of thermal overcoat and have diameters less than 0.5μ.

The functional nanotubes of structure

25 [C_nH_L][R"-R]_m

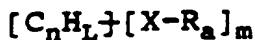
may also be functionalized to produce compositions having the formula

[C_nH_L][R'-A]_m

where n, L, m, R' and A are as defined above. The carbon atoms, C_n, are surface carbons of a substantially cylindrical, graphitic nanotube of substantially constant diameter. The nanotubes include those having a length to diameter ratio of greater than 5 and a diameter of less than 0.5μ, preferably less than 0.1μ. The nanotubes can 30 35 also be substantially cylindrical, graphitic nanotubes which are substantially free of pyrolytically deposited carbon. More preferably they are characterized by having

a projection of the graphite layers on the fibril axes which extends for a distance of at least two fibril diameters and/or by having cylindrical graphitic sheets whose c-axes are substantially perpendicular to their 5 cylindrical axis. Preferably, the nanotubes are free of thermal overcoat and have diameters less than 0.5μ .

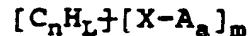
The compositions of the invention also include nanotubes upon which certain cyclic compounds are adsorbed. These include compositions of matter of the 10 formula



where n is an integer, L is a number less than $0.1n$, m is less than $0.5n$, a is zero or a number less than 10, X is a polynuclear aromatic, polyheteronuclear aromatic or 15 metallocopolyheteronuclear aromatic moiety and R is as recited above. The carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic nanotube of substantially constant diameter. The nanotubes include those having a length to diameter ratio of greater than 5 20 and a diameter of less than 0.5μ , preferably less than 0.1μ . The nanotubes can also be substantially cylindrical, graphitic nanotubes which are substantially free of pyrolytically deposited carbon and more 25 preferably those characterized by having a projection of the graphite layers on said fibril axes which extend for a distance of at least two fibril diameters and/or those having cylindrical graphitic sheets whose c-axes are substantially perpendicular to their cylindrical axes. Preferably, the nanotubes are free of thermal overcoat 30 and have diameters less than 0.5μ .

Preferred cyclic compounds are planar macrocycles as described on p. 76 of Cotton and Wilkinson, *Advanced Organic Chemistry*. More preferred cyclic compounds for adsorption are porphyrins and 35 phthalocyanines.

The adsorbed cyclic compounds may be functionalized. Such compositions include compounds of the formula



5 where m, n, L, a, X and A are as defined above and the carbons are surface carbons of a substantially cylindrical graphitic nanotube as described above.

The carbon fibrils functionalized as described above may be incorporated in a matrix. Preferably, the 10 matrix is an organic polymer (e.g., a thermoset resin such as epoxy, bismaleimide, polyamide, or polyester resin; a thermoplastic resin; a reaction injection molded resin; or an elastomer such as natural rubber, styrene-butadiene rubber, or cis-1,4-polybutadiene); an inorganic 15 polymer (e.g., a polymeric inorganic oxide such as glass), a metal (e.g., lead or copper), or a ceramic material (e.g., Portland cement).

Without being bound to a particular theory, the functionalized fibrils are better dispersed into polymer 20 systems because the modified surface properties are more compatible with the polymer, or, because the modified functional groups (particularly hydroxyl or amine groups) are bonded directly to the polymer as terminal groups. In this way, polymer systems such as polycarbonates, 25 polyurethanes, polyesters or polyamides/imides bond directly to the fibrils making the fibrils easier to disperse with improved adherence.

The invention is also in methods of introducing functional groups onto the surface of carbon fibrils by 30 contacting carbon fibrils with a strong oxidizing agent for a period of time sufficient to oxidize the surface of said fibrils and further contacting said fibrils with a reactant suitable for adding a functional group to the oxidized surface. In a preferred embodiment of the 35 invention, the oxidizing agent is comprised of a solution of an alkali metal chlorate in a strong acid. In other embodiments of the invention the alkali metal chlorate is

sodium chlorate or potassium chlorate. In preferred embodiments the strong acid used is sulfuric acid. Periods of time sufficient for oxidation are from about 0.5 hours to about 24 hours.

5 The invention is also in methods for producing a network of carbon fibrils comprising contacting carbon fibrils with an oxidizing agent for a period of time sufficient to oxidize the surface of the carbon fibrils, contacting the surface-oxidized carbon fibrils with
10 reactant suitable for adding a functional group to the surface of the carbon fibrils, and further contacting the surface-functionalized fibrils with a cross-linking agent effective for producing a network of carbon fibrils. A preferred cross-linking agent is a polyol, polyamine or
15 polycarboxylic acid.

Functionalized fibrils also are useful for preparing rigid networks of fibrils. A well-dispersed, three-dimensional network of acid-functionalized fibrils may, for example, be stabilized by cross-linking the acid
20 groups (inter-fibril) with polyols or polyamines to form a rigid network.

The invention also includes three-dimensional networks formed by linking functionalized fibrils of the invention. These complexes include at least two
25 functionalized fibrils linked by one or more linkers comprising a direct bond or chemical moiety. These networks comprise porous media of remarkably uniform equivalent pore size. They are useful as adsorbents, catalyst supports and separation media.

30 Although the interstices between these fibrils are irregular in both size and shape, they can be thought of as pores and characterized by the methods used to characterize porous media. The size of the interstices in such networks can be controlled by the concentration
35 and level of dispersion of fibrils, and the concentration and chain lengths of the cross-linking agents. Such materials can act as structured catalyst supports and may

be tailored to exclude or include molecules of a certain size. Aside from conventional industrial catalysis, they have special applications as large pore supports for biocatalysts.

5 The rigid networks can also serve as the backbone in biomimetic systems for molecular recognition. Such systems have been described in US Patent No. 5,110,833 and International Patent Publication No. WO93/19844. The appropriate choices for cross-linkers 10 and complexing agents allow for stabilization of specific molecular frameworks.

METHODS OF FUNCTIONALIZING FIBRILS

The uniformly functionalized fibrils of the invention can be directly prepared by sulfonation, 15 electrophilic addition to deoxygenated fibril surfaces or metallation. When arc grown nanofibers are used, they may require extensive purification prior to functionalization. Ebbesen et al. (Nature 367 519 (1994)) give a procedure for such purification.

20 Preferably, the carbon fibrils are processed prior to contacting them with the functionalizing agent. Such processing may include dispersing the fibrils in a solvent. In some instances the carbon fibrils may then be filtered and dried prior to further contact.

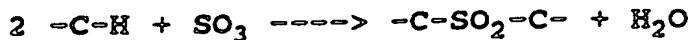
1. SULFONATION

Background techniques are described in March, J.P., *Advanced Organic Chemistry*, 3rd Ed. Wiley, New York 1985; House, H., *Modern Synthetic Reactions*, 2nd Ed., Benjamin/Cummings, Menlo Park, CA 1972.

30 Activated C-H (including aromatic C-H) bonds can be sulfonated using fuming sulfuric acid (oleum), which is a solution of conc. sulfuric acid containing up to 20% SO₃. The conventional method is via liquid phase at T~80°C using oleum; however, activated C-H bonds can 35 also be sulfonated using SO₃ in inert, aprotic solvents, or SO₃ in the vapor phase. The reaction is:



Over-reaction results in formation of sulfones, according to the reaction:



EXAMPLE 1

5 Activation of C-H Bonds Using Sulfuric Acid

Reactions were carried out in the gas phase and in solution without any significant difference in results. The vapor phase reaction was carried out in a horizontal quartz tube reactor heated by a Lindberg furnace. A multi-neck flask containing 20% SO₃ in conc. H₂SO₄ fitted with gas inlet/outlet tubes was used as the SO₃ source.

A weighed sample of fibrils (BN or CC) in a porcelain boat was placed in the 1" tube fitted with a 15 gas inlet; the outlet was connected to a conc. H₂SO₄ bubbler trap. Argon was flushed through the reactor for 20 min to remove all air, and the sample was heated to 300°C for 1 hour to remove residual moisture. After drying, the temperature was adjusted to reaction 20 temperature under argon.

When the desired temperature was stabilized, the SO₃ source was connected to the reactor tube and an argon stream was used to carry SO₃ vapors into the quartz tube reactor. Reaction was carried out for the desired 25 time at the desired temperature, after which the reactor was cooled under flowing argon. The fibrils were then dried at 90°C at 5" Hg vacuum to obtain the dry weight gain. Sulfonic acid (-SO₃H) content was determined by reaction with 0.100N NaOH and back-titration with 0.100N HCl using pH 6.0 as the end point.

The liquid phase reaction was carried out in conc. sulfuric acid containing 20% SO₃ in a multi-neck 100 cc flask fitted with a thermometer/temperature controller and a magnetic stirrer. A fibril slurry in 35 conc. H₂SO₄ (50) was placed in the flask. The oleum solution (20 cc) was preheated to -60°C before addition to the reactor. After reaction, the acid slurry was

10 poured onto cracked ice, and diluted immediately with 1 l DI water. The solids were filtered and washed exhaustively with DI water until there was no change in pH of the wash effluent. Fibrils were dried at 100°C at 5 5" Hg vacuum. Due to transfer losses on filtration, accurate weight gains could not be obtained. Results are listed in Table 1.

TABLE I

10

Summary of Reactions

EX.	RUN #	REACT	SAMPLE Wt.g	FIBRIL TYPE	T°C	TIME	DRY WT GAIN	SO ₃ H CONC meq/g
	1A	118-60A	Vap	0.20	CY	110	15 m	9.3% 0.50
	1B	118-61A	Vap	0.20	BN	100	30 m	8.5% 0.31
15	1C	118-61B	Vap	0.20	BN	65	15 m	4.2% 0.45
	1D	118-56A	Liq	1.2	CY	50	10 m	0.33
	1E	118-56B	Liq	1.0	CY	25	20 m	0.40

20 There was no significant difference in sulfonic acid content by reaction in the vapor phase or liquid phase. There was a temperature effect. Higher temperature of reaction (vapor phase) gives higher amounts of sulfones. In 118-61B, the 4.2% wt gain agreed with the sulfonic acid content (theoretical was 0.51 meq/g). Runs 60A and 61A had too high a wt gain to be accounted for solely by sulfonic acid content. It was therefore assumed that appreciable amounts of sulfones were also made.

2. ADDITIONS TO OXIDE-FREE FIBRIL SURFACES

30 Background techniques are described in Urry, G., *Elementary Equilibrium Chemistry of Carbon*, Wiley, New York 1989.

35 The surface carbons in fibrils behave like graphite, i.e., they are arranged in hexagonal sheets containing both basal plane and edge carbons. While basal plane carbons are relatively inert to chemical attack, edge carbons are reactive and must contain some heteroatom or group to satisfy carbon valency. Fibrils

also have surface defect sites which are basically edge carbons and contain heteroatoms or groups.

The most common heteroatoms attached to surface carbons of fibrils are hydrogen, the predominant gaseous component during manufacture; oxygen, due to its high reactivity and because traces of it are very difficult to avoid; and H₂O, which is always present due to the catalyst. Pyrolysis at ~1000°C in a vacuum will deoxygenate the surface in a complex reaction with unknown mechanism, but with known stoichiometry. The products are CO and CO₂, in a 2:1 ratio. The resulting fibril surface contains radicals in a C₁-C₄ alignment which are very reactive to activated olefins. The surface is stable in a vacuum or in the presence of an inert gas, but retains its high reactivity until exposed to a reactive gas. Thus, fibrils can be pyrolyzed at ~1000°C in vacuum or inert atmosphere, cooled under these same conditions and reacted with an appropriate molecule at lower temperature to give a stable functional group.

20 Typical examples are:

1000°C

Fibril-O -----> Reactive Fibril Surface (RFS) + 2 CO + CO₂

followed by:

25 RFS + CH₂=CHCOX -----> Fibril-R'COX X=-OH, -Cl, -NH₂, -H

RFS + Maleic anhydride -----> Fibril-R'(COOH)₂

RFS + Cyanogen -----> Fibril-CN

30 RFS + CH₂=CH-CH₂X -----> Fibril-R'CH₂X X=-NH₂, -OH, -Halogen,

RFS + H₂O -----> Fibril=O (quinoidal)

RFS + CH₂=CHCHO -----> Fibril-R'CHO (aldehydic)

RFS + CH₂=CH-CN -----> Fibril-R'CN

35

where R' is a hydrocarbon radical (alkyl, cycloalkyl, etc.)

EXAMPLE 2

**Preparation of Functionalized Fibrils by Reacting
Acrylic Acid with Oxide-Free Fibril Surfaces**

One gram of BN fibrils in a porcelain boat is placed in a horizontal 1" quartz tube fitted with a 5 thermocouple and situated in a Lindberg tube furnace. The ends are fitted with a gas inlet/outlets. The tube is purged with dry, deoxygenated argon for 10 minutes, after which the temperature of the furnace is raised to 300°C and held for 30 minutes. Thereafter, under a 10 continued flow of argon, the temperature is raised in 100°C increments to 1000°C, and held there for 16 hours. At the end of that time, the tube is cooled to room temperature (RT) under flowing argon. The flow of argon is then shunted to pass through a multi-neck flask 15 containing neat purified acrylic acid at 50°C and fitted with gas inlet/outlets. The flow of acrylic acid/argon vapors is continued at RT for 6 hours. At the end of that time, residual unreacted acrylic acid is removed, first by purging with argon, then by vacuum drying at 20 100°C at <5" vacuum. The carboxylic acid content is determined by reaction with excess 0.100N NaOH and back-titrating with 0.100N HCl to an endpoint at pH 7.5.

EXAMPLE 3

25 **Preparation of Functionalized Fibrils by Reacting
Acrylic Acid with Oxide-Free Fibril Surfaces**

The procedure is repeated in a similar manner to the above procedure, except that the pyrolysis and cool-down are carried out at 10^{-4} Torr vacuum. Purified acrylic acid vapors are diluted with argon as in the 30 previous procedure.

EXAMPLE 4

**Preparation of Functionalized Fibrils by Reacting
Maleic Acid with Oxide-Free Fibril Surfaces**

The procedure is repeated as in Ex.2, except 35 that the reactant at RT is purified maleic anhydride (MAN) which is fed to the reactor by passing argon gas through a molten MAN bath at 80°C.

EXAMPLE 5Preparation of Functionalized Fibrils by Reacting
Acryloyl Chloride with Oxido-Free Fibril Surfaces

The procedure is repeated as in Ex. 2, except
5 that the reactant at RT is purified acryloyl chloride,
which is fed to the reactor by passing argon over neat
acryloyl chloride at 25°C. Acid chloride content is
determined by reaction with excess 0.100N NaOH and back-
titration with 0.100N HCl.

10 Pyrolysis of fibrils in vacuum deoxygenates the
fibril surface. In a TGA apparatus, pyrolysis at 1000°C
either in vacuum or in a purified Ar flow gives an
average wt loss of 3% for 3 samples of BN fibrils. Gas
chromatographic analyses detected only CO and CO₂, in
15 ~2:1 ratio, respectively. The resulting surface is very
reactive and activated olefins such as acrylic acid,
acryloyl chloride, acrylamide, acrolein, maleic
anhydride, allyl amine, allyl alcohol or allyl halides
will react even at room temperature to form clean
20 products containing only that functionality bonded to the
activated olefin. Thus, surfaces containing only
carboxylic acids are available by reaction with acrylic
acid or maleic anhydride; surf only acid chloride by
reaction with acryloyl chloride; only aldehyde from
25 acrolein; only hydroxyl from allyl alcohol; only amine
from allyl amine, and only halide from allyl halide.

3. METALLATION

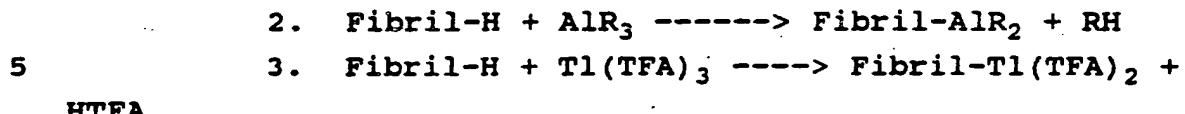
Background techniques are given in March, Advanced
Organic Chemistry, 3rd ed., p 545

30 Aromatic C-H bonds can be metallated with a
variety of organometallic reagents to produce carbon-
metal bonds (C-M). M is usually Li, Be, Mg, Al, or Tl;
however, other metals can also be used. The simplest
reaction is by direct displacement of hydrogen in
35 activated aromatics:



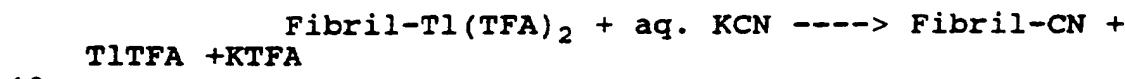
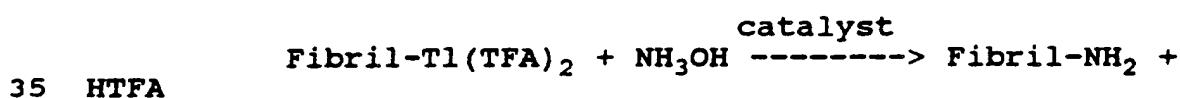
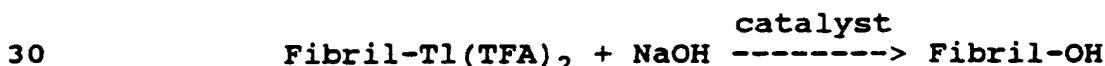
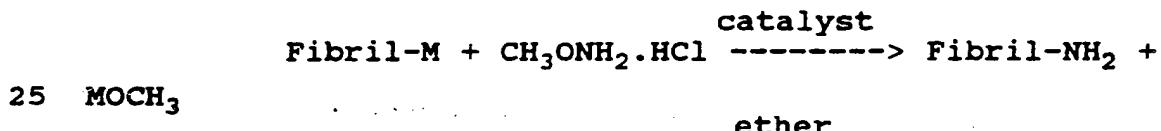
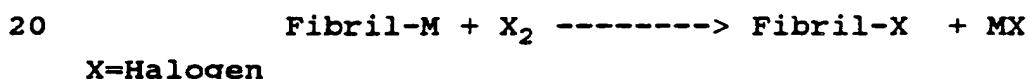
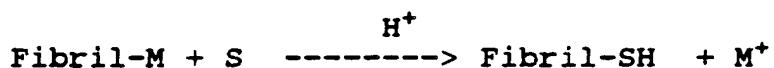
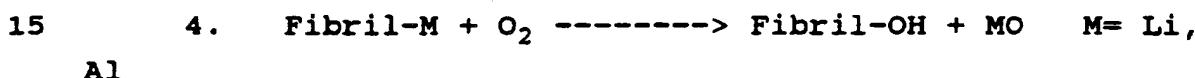
20

The reaction may require additionally, a strong base, such as potassium t-butoxide or chelating diamines. Aprotic solvents are necessary (paraffins, benzene).



TFA=Trifluoroacetate HTFA=Trifluoroacetic acid

10 The metallated derivatives are examples of primary singly-functionalized fibrils. However, they can be reacted further to give other primary singly-functionalized fibrils. Some reactions can be carried out sequentially in the same apparatus without isolation of intermediates.



EXAMPLE 6

Preparation of Fibril-Li

One gram of CC fibrils is placed in a porcelain boat and inserted into a 1" quartz tube reactor which is 5 enclosed in a Lindberg tube furnace. The ends of the tube are fitted with gas inlet/outlets. Under continuous flow of H₂, the fibrils are heated to 700°C for 2 hours to convert any surface oxygenates to C-H bonds. The reactor is then cooled to RT under flowing H₂.

10 The hydrogenated fibrils are transferred with dry, de-oxygenated heptane (with LiAlH₄) to a 1 liter multi-neck round bottom flask equipped with a purified argon purging system to remove all air and maintain an inert atmosphere, a condenser, a magnetic stirrer and 15 rubber septum through which liquids can be added by a syringe. Under an argon atmosphere, a 2% solution containing 5 mmol butyllithium in heptane is added by syringe and the slurry stirred under gentle reflux for 4 hours. At the end of that time, the fibrils are 20 separated by gravity filtration in an argon atmosphere glove box and washed several times on the filter with dry, deoxygenated heptane. Fibrils are transferred to a 50 cc r.b. flask fitted with a stopcock and dried under 10⁻⁴ torr vacuum at 50°C. The lithium concentration is 25 determined by reaction of a sample of fibrils with excess 0.100N HCl in DI water and back-titration with 0.100N NaOH to an endpoint at pH 5.0.

EXAMPLE 7Preparation of Fibril-Tl(TFA)₂

30 One gram of CC fibrils are hydrogenated as in Ex. 5 and loaded into the multi-neck flask with HTFA which has been degassed by repeated purging with dry argon. A 5% solution of 5 mmol Tl(TFA)₂ in HTFA is added to the flask through the rubber septum and the slurry is 35 stirred at gentle reflux for 6 hours. After reaction, the fibrils are collected and dried as in Ex. 1.

EXAMPLE 8

**Preparation of Fibril-OH
(Oxygenated derivative containing only OH
functionalization)**

One half g of lithiated fibrils prepared in

5 Ex. 6 are transferred with dry, deoxygenated heptane in an argon-atmosphere glove bag to a 50 cc single neck flask fitted with a stopcock and magnetic stirring bar. The flask is removed from the glove bag and stirred on a magnetic stirrer. The stopcock is then opened to the air

10 and the slurry stirred for 24 hours. At the end of that time, the fibrils are separated by filtration and washed with aqueous MeOH, and dried at 50°C at 5" vacuum. The concentration of OH groups is determined by reaction with a standardized solution of acetic anhydride in dioxane

15 (0.252 M) at 80°C to convert the OH groups to acetate esters, in so doing, releasing 1 equivalent of acetic acid/mole of anhydride reacted. The total acid content, free acetic acid and unreacted acetic anhydride, is determined by titration with 0.100N NaOH to an endpoint

20 at pH 7.5.

EXAMPLE 9

Preparation of Fibril-NH₂

One gram of thallated fibrils is prepared as in

Ex. 7. The fibrils are slurried in dioxane and 0.5 g

25 triphenyl phosphine dissolved in dioxane is added. The slurry is stirred at 50°C for several minutes, followed by addition at 50°C of gaseous ammonia for 30 min. The fibrils are then separated by filtration, washed in dioxane, then DI water and dried at 80°C at 5" vacuum.

30 The amine concentration is determined by reaction with excess acetic anhydride and back-titration of free acetic acid and unreacted anhydride with 0.100N NaOH.

**4. DERIVATIZED POLYNUCLEAR AROMATIC, POLYHETERONUCLEAR
AROMATIC AND PLANAR MACROCYCLIC COMPOUNDS**

35 The graphitic surfaces of fibrils allow for physical adsorption of aromatic compounds. The attraction is through van der Waals forces. These forces

are considerable between multi-ring heteronuclear aromatic compounds and the basal plane carbons of graphitic surfaces. Desorption may occur under conditions where competitive surface adsorption is possible or where the adsorbate has high solubility.

EXAMPLE 10

Adsorption of Porphyrins and phthalocyanines onto Fibrils

The preferred compounds for physical adsorption on fibrils are derivatized porphyrins or phthalocyanines which are known to adsorb strongly on graphite or carbon blacks. Several compounds are available, e.g., a tetracarboxylic acid porphyrin, cobalt (II) phthalocyanine or dilithium phthalocyanine. The latter two can be derivatized to a carboxylic acid form.

The loading capacity of the porphyrin or phthalocyanines can be determined by decoloration of solutions when they are added incrementally. The deep colors of the solutions (deep pink for the tetracarboxylic acid porphyrin in MeOH, dark blue-green for the Co(II) or the dilithium phthalocyanine in acetone or pyridine) are discharged as the molecules are removed by adsorption onto the black surface of the fibrils.

Loading capacities were estimated by this method and the footprints of the derivatives were calculated from their approximate measurements (~140 sq. Angstroms). For an average surface area for fibrils of $250 \text{ m}^2/\text{g}$, maximum loading will be ~0.3 mmol/g.

The tetracarboxylic acid porphyrin was analyzed by titration. The integrity of the adsorption was tested by color release in aqueous systems at ambient and elevated temperatures.

The fibril slurries were initially mixed (Waring blender) and stirred during loading. Some of the slurries were ultra-sounded after color was no longer discharged, but with no effect.

After loading, Runs 169-11, -12, -14 and -19-1 (see Table II) were washed in the same solvent to remove

occluded pigment. All gave a continuous faint tint in the wash effluent, so it was difficult to determine the saturation point precisely. Runs 168-18 and -19-2 used the calculated amounts of pigment for loading and were 5 washed only very lightly after loading.

The tetracarboxylic acid porphyrin (from acetone) and the Co phthalocyanine (from pyridine) were loaded onto fibrils for further characterization (Runs 169-18 and -19-2, respectively).

10 Analysis of Tetracarboxylic Acid Porphyrin

Addition of excess base (pH 11-12) caused an immediate pink coloration in the titrating slurry. While this did not interfere with the titration, it showed that at high pH, porphyrin desorbed. The carboxylic acid 15 concentration was determined by back titration of excess NaOH using Ph 7.5 as end-point. The titration gave a loading of 1.10 meq/g of acid, equivalent to 0.275 meq/g porphyrin.

Analysis of Cobalt or Dilithium Phthalocyanine

20 The concentrations of these adsorbates were estimated from decoloration experiments only. The point where the blue-green tint did not fade after 30 min was taken as the saturation-point.

A number of substituted polynuclear aromatic or 25 polyheteronuclear aromatic compounds were adsorbed on fibril surfaces. For adhesion, the number of aromatic rings should be greater than two per rings/pendant functional group. Thus, substituted anthracenes, phenanthrenes, etc., containing three fused rings, or 30 polyfunctional derivatives containing four or more fused rings can be used in place of the porphyrin or phthalocyanine derivatives. Likewise, substituted aromatic heterocycles such as the quinolines, or multiply substituted heteroaromatics containing four or more rings 35 can be used.

Table II summarizes the results of the loading experiments for the three porphyrin/phthalocyanine derivatives.

TABLE II

Summary of Adsorption Runs

5

EX.	RUN #	Adsorbate	Wgt.	Fib.a	Solv.	Loading		meq/g Titration
						a/a	Form	
10A	169-11	TCAPorph	19.6 mg	Acet		0.18g/g	Acid	na
10B	169-12	TCAPorph	33.3 mg	H ₂ O		0.11	Na Salt	na
10	10C	169-14	DiLiPhth	119.0 mg	Acet	0.170	Li	na
	10D	169-19-1	CoPhth	250.0 mg	Pyr	0.187	Co	0.335(cal)
	10E	169-18	TCAPorph	1.00 g	Acet	0.205	Acid	1.10(T)
	10F	169-19-2	CoPhth	1.40 g	Pyr	0.172	Co	0.303(cal)

15 TCAPorph=Tetracarboxylic Acid Porphyrin
(cal)=calculated

DiLiPhth=Dilithium Phthalocyanine

(T)=Titration

CoPhth=Cobalt(II) Phthalocyanine

5. CHLORATE OR NITRIC ACID OXIDATION

20 Literature on the oxidation of graphite by strong oxidants such as potassium chlorate in conc. sulfuric acid or nitric acid, includes R.N. Smith, Quarterly Review 13, 287 (1959); M.J.D. Low, Chem. Rev. 60, 267 (1960)). Generally, edge carbons (including 25 defect sites) are attacked to give mixtures of carboxylic acids, phenols and other oxygenated groups. The mechanism is complex involving radical reactions.

EXAMPLE 11

30 Preparation of Carboxylic Acid-Functionalized Fibrils Using Chlorate.

The sample of CC fibrils was slurried in conc. H₂SO₄ by mixing with a spatula and then transferred to a reactor flask fitted with gas inlet/outlets and an 35 overhead stirrer. With stirring and under a slow flow of argon, the charge of NaClO₃ was added in portions at RT over the duration of the run. Chlorine vapors were generated during the entire course of the run and were

swept out of the reactor into a aqueous NaOH trap. At the end of the run, the fibril slurry was poured over cracked ice and vacuum filtered. The filter cake was then transferred to a Soxhlet thimble and washed in a 5 Soxhlet extractor with DI water, exchanging fresh water every several hours. Washing was continued until a sample of fibrils, when added to fresh DI water, did not change the pH of the water. The fibrils were then separated by filtration and dried at 100°C at 5" vacuum 10 overnight.

The carboxylic acid content was determined by reacting a sample with excess 0.100N NaOH and back-titrating with 0.100ⁿ HCl to an endpoint at pH 7.5. The results are listed in the Table.

15

TABLE III
Summary of Direct Oxidation Runs

			<u>Components, g</u>			<u>Time</u>		
20	Rec Acid, Ex. RUN #		Fibrils	NaClO ₃ , cc	H ₂ SO ₄	hours	Wash Ph	Wgt
		<u>meg/g</u>						
	11A	168-30	10.0	8.68		450	24	5.7
25	10.0	0.78						
	11B	168-36	12.0	13.9		600	24	5.9
		13.7	0.75					

30

EXAMPLE 12

**Preparation of Carboxylic Acid-Functionalized
Fibrils Using Nitric Acid.**

A weighed sample of fibrils was slurried with 35 nitric acid of the appropriate strength in a bound bottom multi-neck indented reactor flask equipped with an overhead stirrer and a water condenser. With constant stirring, the temperature was adjusted and the reaction carried out for the specified time. Brown fumes were 40 liberated shortly after the temperature exceeded 70°C, regardless of acid strength. After the reaction, the slurry was poured onto cracked ice and diluted with DI water. The slurry was filtered and excess acid removed

by washing in a Soxhlet extractor, replacing the reservoir with fresh DI water every several hours, until a slurried sample gave no change in Ph from DI water. The fibrils were dried at 100°C at 5" vacuum overnight.

5 A weighed portion of fibrils was reacted with standard 0.100 N NaOH and the carboxylic acid content determined by back-titration with 0.100 N HCl. Surface oxygen content was determined by XPS. Dispersibility in water was tested at 0.1 wt% by mixing in a Waring Blender at

10 high for 2 min. Results are summarized in Table 4.

TABLE IV

Summary of Direct Oxidation Runs

15	COMPONENTS				Temp.	Wgt.	COOH	ESCA, at%								
	Gms.	cc	Acid	Disp.				Ex.	Fibrils	Conc.	°C	Time	Loss	meq/g	C	O
20				H ₂ O												
12A	1(BN)	300	70%	P	RT	24 hr	0	<0.1			98		2			
12B	1(BN)	300	15	P	rflx	48	<5%	<0.1			not analyzed					
12C	20(BN)	1.0 l	70	G	rflx	7	25%	0.8			not analyzed					
12D	48(BN)	1.0 l	70	G	rflx	7	20%	0.9			not analyzed					

P=Poor; G=Good

35 6. SECONDARY DERIVATIVES OF FUNCTIONALIZED FIBRILS
Carboxylic Acid-functionalized Fibrils

The number of secondary derivatives which can be prepared from just carboxylic acid is essentially limitless. Alcohols or amines are easily linked to acid to give stable esters or amides. If the alcohol or amine is part of a di- or poly-functional molecule, then linkage through the O- or NH- leaves the other functionalities as pendant groups. Typical examples of secondary reagents are:

	<u>GENERAL FORMULA</u>	<u>PENDANT GROUP</u>	<u>EXAMPLES</u>
5	HO-R, R=alkyl, aralkyl, aryl, fluoroethanol, polymer, SiR' ₃	R-	Methanol, phenol, trifluorocarbon, OH-terminated Polyester, silanols
	H ₂ N-R R=same as above	R-	Amines, anilines, fluorinated amines, silylamines, amine terminated polyamides
10	Cl-SiR ₃	SiR ₃ -	Chlorosilanes
	HO-R-OH, R=alkyl, aralkyl, CH ₂ O-	HO-	Ethyleneglycol, PEG, Pentaerythritol, bis-Phenol A
15	H ₂ N-R-NH ₂ , R=alkyl, aralkyl	H ₂ N-	Ethylenediamine, polyethyleneamines
20	X-R-Y, R=alkyl, etc; X=OH or NH ₂ ; Y=SH, CN, C=O, CHO, alkene, alkyne, aromatic, heterocycles	Y-	Polyamine amides, Mercaptoethanol

The reactions can be carried out using any of the methods developed for esterifying or aminating carboxylic acids with alcohols or amines. Of these, the methods of H.A. Staab, *Angew. Chem. Internat. Edit.*, (1), 351 (1962) using N,N'-carbonyl diimidazole (CDI) as the acylating agent for esters or amides, and of G.W. Anderson, et al., *J. Amer. Chem. Soc.* 86, 1839 (1964), using N-Hydroxysuccinimide (NHS) to activate carboxylic acids for amidation were used.

EXAMPLE 13

Preparation of Secondary Derivatives of Functionalized Fibrils

35 N, N'-Carbonyl Diimidazole

Clean, dry, aprotic solvents (e.g., toluene or dioxane) are required for this procedure.

Stoichiometric amounts of reagents are sufficient. For esters, the carboxylic acid compound is reacted in an

40 inert atmosphere (argon) in toluene with a stoichiometric

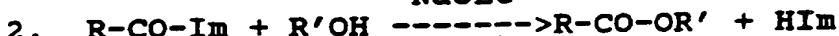
amount of CDI dissolved in toluene at R.T. for 2 hours. During this time, CO_2 is evolved. After two hours, the alcohol is added along with catalytic amounts of Na ethoxide and the reaction continued at 80°C for 4 hr.

5 For normal alcohols, the yields are quantitative. The reactions are:



10

NaOEt



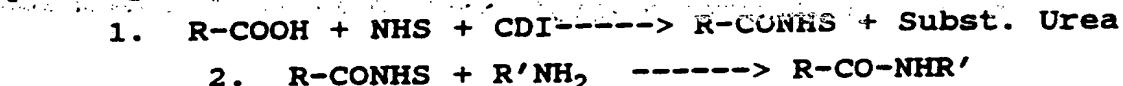
Amidation of amines occurs uncatalyzed at RT.

15 The first step in the procedure is the same. After evolution of CO_2 , a stoichiometric amount of amine is added at RT and reacted for 1-2 hours. The reaction is quantitative. The reaction is:



20 N-Hydroxysuccinimide

Activation of carboxylic acids for amination with primary amines occurs through the N-hydroxysuccinamyl ester; carbodiimide is used to tie up the water released as a substituted urea. The NHS ester is then converted at RT to the amide by reaction with primary amine. The reactions are:



Silylation

30 Trialkylsilylchlorides or trialkylsilanols react immediately with acidic H according to:



Small amounts of Diaza-1,1,1-bicyclooctane (DABCO) are used as catalysts. Suitable solvents are 35 dioxane and toluene.

EXAMPLE 14

**Preparation of Ester/Alcohol Derivatives
from Carboxylic Acid-Functionalized Fibrils**

The carboxylic acid functionalized fibrils were 40 prepared as in Example 11. The carboxylic acid content

was 0.75 meq/g. Fibrils were reacted with a stoichiometric amount of CDI in an inert atmosphere with toluene as solvent at R.T. until CO₂ evolution ceased. Thereafter, the slurry was reacted at 80 °C with a 10-fold molar excess of polyethyleneglycol (MW 600) and a small amount of NaOEt as catalyst. After two hours reaction, the fibrils were separated by filtration, washed with toluene and dried at 100 °C.

EXAMPLE 15

10 Preparation of Amide/Amine Derivatives
from Carboxylic Acid-Functionalized Fibrils (177-041-1)

0.242 g of chlorate-oxidized fibrils (0.62 meq/g) was suspended in 20 ml anhydrous dioxane with stirring in a 100 ml RB flask fitted with a serum stopper. A 20-fold molar excess of N-Hydroxysuccinimide (0.299 g) was added and allowed to dissolve. This was followed by addition of 20-fold molar excess of 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDAC) (0.510 g), and stirring was continued for 2 hr at RT. At the end of this period stirring was stopped, and the supernatant aspirated and the solids were washed with anhydrous dioxane and MeOH and filtered on a 0.45 micron polysulfone membrane. The solids were washed with additional MeOH on the filter membrane and vacuum-dried until no further weight reduction was observed. Yield of NHS-activated oxidized fibrils was 100% based on the 6% weight gain observed.

100 µl ethylenediamine (en) was added to 10 ml 0.2 M NaHCO₃ buffer. An equivalent volume of acetic acid (HOAc) was added to maintain the pH near 8. NHS-activated oxidized fibrils (0.310 g) was added with vigorous stirring and reacted for 1 hr. An additional 300 µl of en and 300 µl HOAc was added for an additional 10 min. The solution was filtered on 0.45 micron polysulfone membrane and washed successively with NaHCO₃ buffer, 1% HCl, DI water and EtOH. The solids were dried under vacuo overnight. The HCl salt was converted back

to the free amine by reaction with NaOH (177-046-1) for further analysis and reactions.

ESCA was carried out to quantify the amount of N present on the aminated fibrils (GF/NH₂). ESCA analysis of 177-046-1 showed 0.90 at% N (177-059). To further assess how much of this N is present as both accessible and reactive amine groups, a derivative was made by the gas phase reaction with pentafluorobenzaldehyde to produce the corresponding Schiff Base linkages with available primary amine groups. ESCA analysis still showed the 0.91 at% N, as expected, and 1.68 at% F. This translates into a 0.34 at% of N present as reactive primary amine on the aminated fibrils (5 F per pentafluorobenzaldehyde molecule). A level of 0.45 at% N would be expected assuming complete reaction with the free ends of each N. The observed level indicates a very high yield from the reaction of N with NHS-activated fibril and confirms the reactivity of the available free amine groups.

At the level of 0.34 at% N present as free amine calculated from the ESCA data, there would be almost complete coverage of the fibrils by the free amine groups allowing coupling of other materials.

EXAMPLE 16

Preparation of Silyl Derivative
from Carboxylic Acid-Functionalized Fibrils

Acid functionalized fibrils prepared as in Example 11 were slurried in dioxane in an inert atmosphere. With stirring, a stoichiometric amount of 30 chlorotriethyl silane was added and reacted for 0.5 hr, after which several drops of a 5% solution of DABCO in dioxane was added. The system was reacted for an additional hour, after which the fibrils were collected by filtration and washed in dioxane. The fibrils were 35 dried at 100°C in 5" vacuum overnight.

Table 5 summarizes the secondary derivative preparations. The products were analyzed by ESCA for C, O, N, Si and F surface contents.

TABLE V

5

Summary of Secondary Derivative Preparations

	<u>REACTANT</u>	<u>PENDANT GROUP</u>	<u>S</u>	ESCA ANALYSIS, ATOM %				
				C	N	O	Si	F
	As Grown	-----	--	98.5	--	1.5	--	--
10	Chlorate Oxidized	-COOH, C=O, C-OH	--	92.4	--	7.6	--	--
	$\text{H}_2\text{N}-\text{C}_2\text{H}_4-\text{NH}_2$	-CONHC ₂ H ₄ NH ₂	--	99.10	0.90	--	--	--
15		-CONHC ₂ H ₄ N=OC ₆ F ₅	--	97.41	0.91	--	--	1.6

EXAMPLE 17

20

Preparation of Silyl Derivative
from Carboxylic Acid-Functionalized Fibrils

Acid functionalized fibrils prepared as in Example 11 are slurried in dioxane in an inert atmosphere. With stirring, a stoichiometric amount of 25 chlorotriethyl silane is added and reacted for 0.5 hr, after which several drops of a 5% solution of DABCO in dioxane is added. The system is reacted for an additional hour, after which the fibrils are collected by filtration and washed in dioxane. The fibrils are dried 30 at 100°C in 5" vacuum overnight.

Table VI summarizes the secondary derivative preparations. Products are analyzed by ESCA. The analysis confirms the incorporation of the desired pendant groups. The products are analyzed by ESCA for C, 35 O, N, Si and F surface contents.

TABLE VI

Summary of Secondary Derivative Preparations

5	REACTANT	PENDANT GROUP	ESCA ANALYSIS, ATOM %				
			S	C	N	O	Si
	CF ₃ CH ₂ OH	-COOCH ₂ CF ₃					NOT ANALYZED
10	PolyEG-600	-CO-(OC ₂ H ₄ O-)-H					NOT ANALYZED
	HO-C ₂ H ₄ -SH	-COOC ₂ H ₄ SH					
	Cl-SiEt ₃	-COSiEt ₃					

15 Sulfonic Acid-Functionalized Fibrils

Aryl sulfonic acids, as prepared in Example 1 can be further reacted to yield secondary derivatives. Sulfonic acids can be reduced to mercaptans by LiAlH₄ or the combination of triphenyl phosphine and iodine (March, 20 J.P., p. 1107). They can also be converted to sulfonate esters by reaction with dialkyl ethers, i.e., Fibril--SO₃H + R-O-R ----> Fibril-SO₂OR + ROH

Fibrils Functionalized by Electrophilic Addition to Oxygen-

25 Free Fibril Surfaces or by Metallization

The primary products obtainable by addition of activated electrophiles to oxygen-free fibril surfaces have pendant -COOH, -COCl, -CN, -CH₂NH₂, -CH₂OH, -CH₂-Halogen, or HC=O. These can be converted to secondary derivatives by the following:

Fibril-COOH ----> see above.

Fibril-COCl (acid chloride) + HO-R-Y ----> F-COO-R-Y
(Sec. 4/5)

Fibril-COCl + NH₂-R-Y -----> F-CONH-R-Y

35 Fibril-CN + H₂ -----> F-CH₂-NH₂
Fibril-CH₂NH₂ + HOOC-R-Y ----> F-CH₂NHCO-R-Y
Fibril-CH₂NH₂ + O=CR-R'Y ----> F-CH₂N=CR-R'-Y
Fibril-CH₂OH + O(COR-Y)₂ -----> F-CH₂OCOR-Y
Fibril-CH₂OH + HOOC-R-Y -----> F-CH₂OCOR-Y
40 Fibril-CH₂-Halogen + Y⁻ -----> F-CH₂-Y + X⁻ Y⁻ = NCO⁻, -OR⁻
Fibril-C=O + H₂N-R-Y -----> F-C=N-R-Y

Fibrils Functionalized by Adsorption of Polynuclear or Polyheteronuclear Aromatic or Planar Macrocyclic Compounds

Dilithium phthalocyanine: In general, the two 5 Li^+ ions are displaced from the phthalocyanine (Pc) group by most metal (particularly multi-valent) complexes. Therefore, displacement of the Li^+ ions with a metal ion bonded with non-labile ligands is a method of putting stable functional groups onto fibril surfaces. Nearly 10 all transition metal complexes will displace Li^+ from Pc to form a stable, non-labile chelate. The point is then to couple this metal with a suitable ligand.

Cobalt (II) Phthalocyanine

Cobalt (II) complexes are particularly suited 15 for this. Co^{++} ion can be substituted for the two Li^+ ions to form a very stable chelate. The Co^{++} ion can then be coordinated to a ligand such as nicotinic acid, which contains a pyridine ring with a pendant carboxylic acid group and which is known to bond preferentially to the 20 pyridine group. In the presence of excess nicotinic acid, Co(II)Pc can be electrochemically oxidized to Co(III)Pc , forming a non-labile complex with the pyridine moiety of nicotinic acid. Thus, the free carboxylic acid group of the nicotinic acid ligand is firmly attached to 25 the fibril surface.

Other suitable ligands are the aminopyridines or ethylenediamine (pendant NH_2), mercaptopyridine (SH), or other polyfunctional ligands containing either an amino- or pyridyl- moiety on one end, and any desirable 30 function on the other.

7. 3-DIMENSIONAL STRUCTURES

The oxidized fibrils are more easily dispersed in aqueous media than unoxidized fibrils. Stable, porous 3-dimensional structures with meso- and macropores (pores 35 >2 nm) are very useful as catalysts or chromatography supports. Since fibrils can be dispersed on an individualized basis, a well-dispersed sample which is

stabilized by cross-links allows one to construct such a support. Functionalized fibrils are ideal for this application since they are easily dispersed in aqueous or polar media and the functionality provides cross-link 5 points. Additionally, the functionality provides points to support the catalytic or chromatographic sites. The end result is a rigid, 3-dimensional structure with its total surface area accessible with functional sites on which to support the active agent.

10 Typical applications for these supports in catalysis include their use as a highly porous support for metal catalysts laid down by impregnation, e.g., precious metal hydrogenation catalysts. Moreover, the ability to anchor molecular catalysts by tether to the 15 support via the functionality combined with the very high porosity of the structure allows one to carry out homogeneous reactions in a heterogeneous manner. The tethered molecular catalyst is essentially dangling in a continuous liquid phase, similar to a homogeneous 20 reactor, in which it can make use of the advantages in selectivities and rates that go along with homogeneous reactions. However, being tethered to the solid support allows easy separation and recovery of the active, and in many cases, very expensive catalyst.

25 These stable, rigid structures also permits carrying out heretofore very difficult reactions, such as asymmetric syntheses or affinity chromatography by attaching a suitable enantiomeric catalyst or selective substrate to the support. Derivatization through 30 Metallo-Pc or Metallo-porphyrin complexes also allows for retrieval of the ligand bonded to the metal ion, and furthermore, any molecule which is bonded to the ligand through the secondary derivatives. For example, in the case where the 3-dimensional structure of functionalized 35 fibrils is an electrode, or part of an electrode, and the functionalization has resulted from adsorption of Co(II)Pc, electrochemical oxidation of Co(II) to Co(III)

in the presence of nicotinic acid will produce a non-labile Co(III)-pyridyl complex with a carboxylic acid as the pendent group. Attaching a suitable antigen, antibody, catalytic antibody, or other site-specific trapping agent will permit selective separations of molecules (affinity chromatography) which are otherwise very difficult to achieve. After washing the electrode to remove occluded material, the Co(III) complex containing the target molecule can be electrochemically reduced to recover the labile Co(II) complex. The ligand on Co(II) containing the target molecule can then be recovered by mass action substitution of the labile Co(II) ligand, thereby effecting a separation and recovery of molecules which are otherwise very difficult or expensive to perform (e.g., chiral drugs).

Another example of 3-dimensional structures are fibril-ceramic composites.

EXAMPLE 18

Preparation of Alumina-Fibril Composites (185-02-01)

One g of nitric acid oxidized fibrils (185-01-02) was highly dispersed in 100 cc DI water using an U/S disintegrator. The fibril slurry was heated to 90°C and a solution of 0.04 mol aluminum tributoxide dissolved in 20 cc propanol was slowly added. Reflux was continued for 4 hr, after which the condenser was removed to drive out the alcohol. After 30 min the condenser was put back and the slurry refluxed at 100°C overnight. A black sol with uniform appearance was obtained. The sol was cooled to RT and after one week, a black gel with a smooth surface was formed. The gel was heated at 300°C in air for 12 hr.

The alumina-fibril composites were examined by SEM. Micrographs of cracked surfaces showed a homogeneous dispersion of fibrils in the gel.

EXAMPLE 19Preparation of Silica-Fibril Composites (173-85-03)

Two g of nitric acid oxidized fibrils (173-83-03) were highly dispersed on 200 cc ethanol using ultrasonification. A solution of 0.1 mol tetraethoxysilane dissolved in 50 cc ethanol was slowly added to the slurry at RT, followed by 3 cc conc. HCL. The mixture was heated to 85°C and maintained at that temperature until the volume was reduced to 100 cc. The mixture was cooled and set aside until it formed a black solid gel. The gel was heated at 300°C in air.

The silica-fibril composites were examined by SEM. Micrographs of cracked surfaces showed a homogeneous dispersion of fibrils in the gel.

Similar preparations with other ceramics, such as zirconia, titania, rare earth oxides as well as ternary oxides can be prepared.

As illustrated by the foregoing description and examples, the invention has application in the formulation of a wide variety of functionalized nanotubes.

The terms and expressions which have been employed are used as terms of description and not of limitations, and there is no intention in the use of such terms or expressions of excluding any equivalents of the features shown and described as portions thereof, its being recognized that various modifications are possible within the scope of the invention.

WHAT IS CLAIMED IS:

1. A composition of matter of the formula



wherein the carbon atoms, C_n , are surface
5 carbons of a substantially cylindrical, graphitic
nanotube having a length to diameter ratio of greater
than 5 and a diameter of less than 0.5 micron,

n is an integer, L is a number less than 0.1n,
m is a number less than 0.5n,

10 each of R is the same and is selected from
 SO_3H , $COOH$, NH_2 , OH , CHO , CN , $COCl$, halide, $COSH$, SH ,
 $COOR'$, SR' , $Si\{OR'\}_yR'^{3-y}$, $Si\{O-SiR'\}_2OR'$, R'' , Li ,
 AlR'^2 , $Hg-X$, TlZ_2 and $Mg-X$, y is an integer equal
to or less than 3,

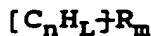
15 R' is alkyl, aryl, cycloalkyl, aralkyl or
cycloaryl,

R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl
or fluoroaralkyl,

X is a halide, and

20 Z is carboxylate or trifluoroacetate.

2. A composition of matter of the formula



wherein the carbon atoms, C_n , are surface
carbons of a substantially cylindrical, graphitic fibril
25 being substantially free of pyrolytically deposited
carbon, the projection of the graphite layers on said
fibrils extends for a distance of at least two fibril
diameters,

n is an integer, L is a number less than 0.1n,
30 m is a number less than 0.5n,

each of R is the same and is selected from
 SO_3H , $COOH$, NH_2 , OH , CHO , CN , $COCl$, halide, $COSH$, SH ,
 $COOR'$, SR' , $Si\{OR'\}_yR'^{3-y}$, $Si\{O-SiR'\}_2OR'$, R'' , Li ,
 AlR'^2 , $Hg-X$, TlZ_2 and $Mg-X$, y is an integer equal
35 to or less than 3,

R' is alkyl, aryl, cycloalkyl, aralkyl or
cycloaryl,

R" is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

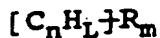
X is a halide, and

Z is carboxylate or trifluoroacetate.

5 3. A composition of matter as claimed in claim 2, wherein said fibril comprises cylindrical graphitic sheets whose c-axes are substantially perpendicular to their cylindrical axis.

10 4. A composition of matter as claimed in claim 2, wherein the outer diameter of said fibrils is less than 0.1 micron.

15 5. A composition of matter of the formula



wherein the carbon atoms, C_n , are surface atoms 15 of a fishbone fibril,

n is an integer, L is a number less than 0.1n, m is a number less than 0.5n,
each of R is the same and is selected from SO₃H, COOH, NH₂, OH, CHO, CN, COCl, halide, COSH, SH, COOR', SR', SiR'₃, Si_yOR'_yR'_{3-y}, Si_yO-SiR'_{2-y}OR', R", Li, AlR'₂, Hg-X, TlZ₂ and Mg-X, y is an integer equal to or less than 3,

20 R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

25 R" is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

X is a halide, and

Z is carboxylate or trifluoroacetate.

30 6. A composition of matter of the formula



wherein the carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic nanotube having a length to diameter ratio of greater than 5 and a diameter of less than 0.5 micron,

35 n is an integer, L is a number less than 0.1n and m is a number less than 0.5n,

each of R is selected from SO₃H, COOH, NH₂, OH, CHO, CN, COCl, halide, COSH, SH, COOR', SR', SiR'₃,

$\text{Si}(\text{OR}')_y\text{R}'_{3-y}$, $\text{Si}(\text{O-SiR}')_2\text{OR}'$, R'' , Li , AlR'_2 , Hg-X , TiZ_2 and Mg-X ,

y is an integer equal to or less than 3,
 R' is selected from alkyl, aryl, cycloalkyl,

5 aralkyl, cycloaryl,

R'' is a fluoroalkyl, fluoroaryl,
 fluorocycloalkyl or fluoroaralkyl,

X is a halide,

Z is carboxylate or trifluoroacetate,

10 and further provided that where each of R is an oxygen-containing group COOH is not present.

7. A composition of matter of the formula



wherein the carbon atoms, C_n , are surface

15 carbons of a substantially cylindrical, graphitic fibril being substantially free of pyrolytically deposited carbon, the projection of the graphite layers on said fibrils extends for a distance of at least two fibril diameters,

20 n is an integer, L is a number less than 0.1n and m is a number less than 0.5n,

each of R is selected from SO_3H , COOH , NH_2 , OH , CHO , CN , COCl , halide, COSH , SH , COOR' , SR' , SiR'_3 , $\text{Si}(\text{OR}')_y\text{R}'_{3-y}$, $\text{Si}(\text{O-SiR}')_2\text{OR}'$, R'' , Li , AlR'_2 , Hg-X , TiZ_2

25 and Mg-X ,

y is an integer equal to or less than 3,
 R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

R'' is a fluoroalkyl, fluoroaryl,

30 fluorocycloalkyl or fluoroaralkyl,

X is a halide,

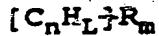
Z is a carboxylate or trifluoroacetate,

and further provided that where each of R is an oxygen-containing group COOH is not present.

35 8. A composition of matter as claimed in claim 7, wherein said fibril comprises cylindrical graphitic sheets whose c-axes are substantially perpendicular to their cylindrical axis.

9. A composition of matter as claimed in claim 7, wherein the outer diameter of said fibrils is less than 0.1 micron.

10. A composition of matter of the formula



5 wherein the carbon atoms, C_n , are surface atoms of a fishbone fibril,

n is an integer, L is a number less than 0.1n and m is a number less than 0.5n,

10 each of R is selected from SO_3H , $COOH$, NH_2 , OH , CHO , CN , $COCl$, halide, $COSH$, SH , $COOR'$, SR' , SiR'_3 , $Si\{OR'\}_yR'^{3-y}$, $Si\{O-SiR'_2\}OR'$, R'' , Li , AlR'_2 , $Hg-X$, TlZ_2 and $Mg-X$,

y is an integer equal to or less than 3,

15 R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

R'' is a fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

X is a halide,

20 Z is a carboxylate or trifluoroacetate,

and further provided that where each of R is an oxygen-containing group $COOH$ is not present.

11. A composition of matter of the formula



25 wherein the carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic nanotube having a length to diameter ratio of greater than 5 and a diameter of less than 0.5 micron,

n is an integer, L is a number less than 0.1n and m is a number less than 0.5n,

30 each of R is selected from SO_3H , $COOH$, NH_2 , OH , CHO , CN , $COCl$, halide, $COSH$, SH , $COOR'$, SR' , SiR'_3 , $Si\{OR'\}_yR'^{3-y}$, $Si\{O-SiR'_2\}OR'$, R'' , Li , AlR'_2 , $Hg-X$, TlZ_2 and $Mg-X$,

35 y is an integer equal to or less than 3,

R' is selected from alkyl, aryl, cycloalkyl, aralkyl, cycloaryl,

R'' is a fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

X is a halide,
Z is carboxylate or trifluoroacetate,
and further provided that each of R does not contain oxygen.

5 12. A composition of matter of the formula



wherein the carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic fibril being substantially free of pyrolytically deposited 10 carbon, the projection of the graphite layers on said fibrils extends for a distance of at least two fibril diameters,

n is an integer, L is a number less than 0.1n and m is a number less than 0.5n,

15 each of R is selected from SO_3H , $COOH$, NH_2 , OH , CHO , CN , $COCl$, halide, $COSH$, SH , $COOR'$, SR' , SiR'_3 , $Si\{OR'\}_yR'^{3-y}$, $Si\{O-SiR'_2\}OR'$, R'' , Li , AlR'_2 , $Hg-X$, TlZ_2 and $Mg-X$,

20 y is an integer equal to or less than 3,
R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

R'' is a fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

25 X is a halide,
Z is a carboxylate or trifluoroacetate,
and further provided that each of R does not contain oxygen.

30 13. A composition of matter as claimed in claim 12, wherein said fibril comprises cylindrical graphitic sheets whose c-axes are substantially perpendicular to their cylindrical axis.

14. A composition of matter as claimed in claim 12, wherein the outer diameter of said fibrils is less than 0.1 micron.

35 15. A composition of matter of the formula



wherein the carbon atoms, C_n , are surface atoms of a fishbone fibril,

n is an integer, L is a number less than 0.1n and m is a number less than 0.5n,

each of R is selected from SO_3H , COOH , NH_2 , OH , CHO , CN , COCl , halide, COSH , SH , COOR' , SR' , SiR'_3 ,
5 $\text{Si}\{\text{OR}'\}_y\text{R}'_{3-y}$, $\text{Si}\{\text{O-SiR}'_2\}\text{OR}'$, R'' , Li , AlR'_2 , Hg-X , TlZ_2 and Mg-X ,

y is an integer equal to or less than 3,
R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

10 R'' is a fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

X is a halide,

Z is a carboxylate or trifluoroacetate,
and further provided that each of R does not

15 contain oxygen.

16. A composition of matter of the formula



wherein the carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic

20 nanotube having a length to diameter ratio of greater than 5 and a diameter of less than 0.1 micron,

n is an integer, L is a number less than 0.1n,

m is a number less than 0.5n,

each of A is selected from

25
$$\begin{array}{c} \text{O} & \text{O} & \text{O} & \text{O} \\ | & | & | & | \\ \text{OY} & \text{NHY} & \text{C-OY} & \text{C-NR}'\text{Y} & \text{C-SY} & \text{C-Y} & -\text{CR}'_2-\text{OY} & \text{N=Y} & \text{C=Y} \end{array}$$

30 Y is an appropriate functional group of a protein, a peptide, an enzyme, an antibody, a nucleotide, an oligonucleotide, an antigen, or an enzyme substrate, enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from $\text{R}'-\text{OH}$, $\text{R}'-\text{NH}_2$, $\text{R}'\text{SH}$,
35 $\text{R}'\text{CHO}$, $\text{R}'\text{CN}$, $\text{R}'\text{X}$, $\text{R}'\text{SiR}'_3$, $\text{R}'\text{Si}\{\text{OR}'\}_y\text{R}'_{3-y}$, $\text{R}'\text{Si}\{\text{O-SiR}'_2\}\text{OR}'$, $\text{R}'-\text{R}''$, $\text{R}'-\text{N-CO}$, $(\text{C}_2\text{H}_4\text{O})_w\text{H}$, $(\text{C}_3\text{H}_6\text{O})_w\text{H}$, $(\text{C}_2\text{H}_4\text{O})_w\text{R}'$, $(\text{C}_3\text{H}_6\text{O})_w\text{R}'$ and R' ,

y is an integer equal to or less than 3,

R' is alkyl, aryl, cycloalkyl, aralkyl or

40 cycloaryl,

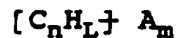
R" is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

X is a halide,

Z is carboxylate or trifluoroacetate, and

5 w is an integer greater than one and less than 200.

17. A composition of matter of the formula



wherein the carbon atoms, C_n , are surface 10 carbons of a substantially cylindrical, graphitic fibril being substantially free of pyrolytically deposited carbon, the projection of the graphite layers on said fibrils extends for a distance of at least two fibril diameters,

15 n is an integer, L is a number less than 0.1n, m is a number less than 0.5n,

each of A is selected from



20 OY, NHY, C-OY, C-NR'Y, C-SY, C-Y, -CR'₂-OY, N=Y, and C=Y,

Y is an appropriate functional group of a protein, a peptide, an enzyme, an antibody, a nucleotide, an oligonucleotide, an antigen, or an enzyme substrate, enzyme inhibitor or the transition state analog of an

25 enzyme substrate or is selected from R'-OH, R'-NH₂, R'SH, R'CHO, R'CN, R'X, R'SiR'₃, R'Si+OR'⁻_yR'₃⁻_y, R'Si+O⁻
SiR'₂⁻OR', R'-R", R'-N-CO, (C₂H₄O)_wH, +(C₃H₆O)_wH, +(C₂H₄O)_w-R', (C₃H₆O)_w-R' and R',

30 y is an integer equal to or less than 3,

R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

R" is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

X is a halide,

35 Z is carboxylate or trifluoroacetate, and w is an integer greater than one and less than 200.

18. A composition of matter as claimed in claim 17, wherein said fibril comprises cylindrical

graphitic sheets whose c-axes are substantially perpendicular to their cylindrical axis.

19. A composition of matter as claimed in claim 17, wherein the outer diameter of said fibrils is 5 less than 0.1 micron.

20. A composition of matter of the formula



wherein the carbon atoms, C_n , are surface atoms of a fishbone fibril,

10 n is an integer, L is a number less than 0.1n, m is a number less than 0.5n, each of A is selected from



15 Y is an appropriate functional group of a protein, a peptide, an enzyme, an antibody, a nucleotide, an oligonucleotide, an antigen, or an enzyme substrate, 20 enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from $R'-OH$, $R'-NH_2$, $R'SH$, $R'CHO$, $R'CN$, $R'X$, $R'SiR'_3$, $R'Si-OR'^+_yR'^{3-y}$, $R'Si-O-SiR'^{2-y}OR'$, $R'-R''$, $R'-N-CO$, $(C_2H_4O)_wH$, $(C_3H_6O)_wH$, $(C_2H_4O)_wR'$, $(C_3H_6O)_wR'$ and R' ,

25 y is an integer equal to or less than 3, R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl, R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

30 X is a halide, Z is carboxylate or trifluoroacetate, and w is an integer greater than one and less than 200.

21. A composition of matter of the formula



35 wherein the carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic nanotube having a length to diameter ratio of greater than 5 and a diameter of less than 0.5 micron,

40 n is an integer, L is a number less than 0.1n, m is a number less than 0.5n,

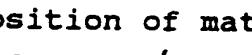
each of R is selected from SO_3H , COOH , NH_2 , OH , CHO , CN , COCl , halide, COSH , SH , COOR' , SR' , SiR'_3 , $\text{Si}(\text{OR}')_y\text{R}'_{3-y}$, $\text{Si}(\text{O-SiR}'_2)\text{OR}'$, R'' , Li , AlR'_2 , Hg-X , TiZ_2 and Mg-X ,

5 y is an integer equal to or less than 3,
 R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

X is a halide,

10 R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl, and

22. A composition of matter of the formula



wherein the carbon atoms, C_n , are surface

15 carbons of a substantially cylindrical, graphitic fibril being substantially free of pyrolytically deposited carbon, the projection of the graphite layers on said fibrils extends for a distance of at least two fibril diameters,

20 n is an integer, L is a number less than 0.1n, m is a number less than 0.5n,

each of R is selected from SO_3H , COOH , NH_2 , OH , CHO , CN , COCl , halide, COSH , SH , COOR' , SR' , SiR'_3 , $\text{Si}(\text{OR}')_y\text{R}'_{3-y}$, $\text{Si}(\text{O-SiR}'_2)\text{OR}'$, R'' , Li , AlR'_2 , Hg-X , TiZ_2 and Mg-X ,

25 y is an integer equal to or less than 3,
 R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

X is a halide,

30 R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl, and

22. A composition of matter as claimed in

claim 22, wherein said fibril comprises cylindrical 35 graphitic sheets whose c-axes are substantially perpendicular to their cylindrical axis.

24. A composition of matter as claimed in claim 22, wherein the outer diameter of said fibrils is less than 0.1 micron.

25. A composition of matter of the formula



wherein the carbon atoms, C_n , are surface atoms of a fishbone fibril,

5 n is an integer, L is a number less than 0.1n,
m is a number less than 0.5n,

each of R is selected from SO_3H , $COOH$, NH_2 , OH ,
 CHO , CN , $COCl$, halide, $COSH$, SH , $COOR'$, SR' , SiR'_3 ,
 $Si\{OR'\}_yR'^{3-y}$, $Si\{O-SiR'_2\}OR'$, R'' , Li , AlR'_2 , $Hg-X$, TlZ_2

10 and $Mg-X$,

y is an integer equal to or less than 3,

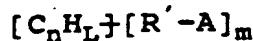
R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

X is a halide,

15 R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl, and

Z is carboxylate or trifluoroacetate.

26. A composition of matter of the formula



20 wherein the carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic nanotube having a length to diameter ratio of greater than 5 and a diameter of less than 0.5 micron,

n is an integer, L is a number less than 0.1n,
25 m is a number less than 0.5n,

each of R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

A is selected from



30 Y is an appropriate functional group of a protein, a peptide, an enzyme, an antibody, a nucleotide, an oligonucleotide, an antigen, or an enzyme substrate, 35 enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from $R'-OH$, $R'-NH_2$, $R'SH$, $R'CHO$, $R'CN$, $R'X$, $R'SiR'_3$, $R'Si\{OR'\}_yR'^{3-y}$, $R'Si\{O-SiR'_2\}OR'$, $R''-R''$, $R''-N-CO$, $(C_2H_4O)_wH$, $(C_3H_6O)_wH$, $(C_2H_4O)_w-$
40 R' , $(C_3H_6O)_w-R'$ and R' ,

y is an integer equal to or less than 3,

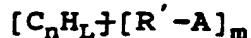
R" is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

X is a halide,

Z is carboxylate or trifluoroacetate, and

5 w is an integer greater than one and less than 200.

27. A composition of matter of the formula



wherein the carbon atoms, C_n, are surface

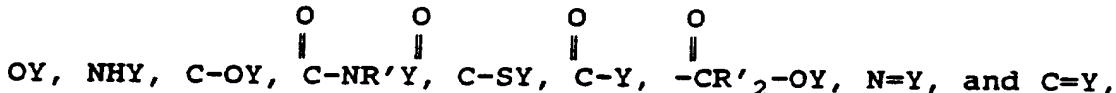
10 carbons of a substantially cylindrical, graphitic fibril being substantially free of pyrolytically deposited carbon, the projection of the graphite layers on said fibrils extends for a distance of at least two fibril diameters,

15 n is an integer, L is a number less than 0.1n, m is a number less than 0.5n,

each of R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

A is selected from

20



Y is an appropriate functional group of a protein, a peptide, an enzyme, an antibody, a nucleotide,

25 an oligonucleotide, an antigen, or an enzyme substrate, enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from R'-OH, R'-NH₂, R'SH, R'CHO, R'CN, R'X, R'SiR'₃, R'Si{OR'}_yR'_{3-y}, R'Si{O-SiR'₂}OR', R'-R", R'-N-CO, (C₂H₄O)_wH, (C₃H₆O)_wH, (C₂H₄O)_w-

30 R', (C₃H₆O)_w-R' and R',

y is an integer equal to or less than 3,

R" is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

X is a halide,

35 Z is carboxylate or trifluoroacetate, and

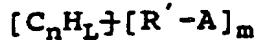
w is an integer greater than one and less than 200.

28. A composition of matter as claimed in claim 27, wherein said fibril comprises cylindrical

graphitic sheets whose c-axes are substantially perpendicular to their cylindrical axis.

29. A composition of matter as claimed in claim 27, wherein the outer diameter of said fibrils is 5 less than 0.1 micron.

30. A composition of matter of the formula



wherein the carbon atoms, C_n , are surface atoms of a fishbone fibril,

10 n is an integer, L is a number less than 0.1n, m is a number less than 0.5n,

each of R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

A is selected from

15
$$\begin{array}{c} O & O & O & O \\ | & | & | & | \\ OY, & NHY, & C-OY, & C-NR'Y, & C-SY, & C-Y, & -CR'_2-OY, & N=Y, & and C=Y, \end{array}$$

Y is an appropriate functional group of a 20 protein, a peptide, an enzyme, an antibody, a nucleotide, an oligonucleotide, an antigen, or an enzyme substrate, enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from $R'-OH$, $R'-NH_2$, $R'SH$, $R'CHO$, $R'CN$, $R'X$, $R'SiR'_3$, $R'Si\{OR'\}_yR'^{3-y}$, $R'Si\{O-$ 25 $SiR'_2\}OR'$, $R'-R''$, $R'-N-CO$, $(C_2H_4O)_wH$, $\{C_3H_6O\}_wH$, $\{C_2H_4O\}_w-$ R' , $(C_3H_6O)_w-R'$ and R' ,

y is an integer equal to or less than 3,

R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

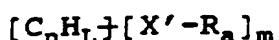
30 X is a halide,

Z is carboxylate or trifluoroacetate, and

w is an integer greater than one and less than

200.

31. A composition of matter of the formula



wherein the carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic nanotube having a length to diameter ratio of greater than 5 and a diameter of less than 0.5 micron,

n is an integer, L is a number less than 0.1n,
 m is a number less than 0.5n, a is zero or an integer
 less than 10,

each of R is selected from SO_3H , COOH , NH_2 , OH ,
 5 CHO , CN , COCl , halide, COSH , SH , COOR' , SR' , SiR'_3 ,
 $\text{Si}(\text{OR}')_y\text{R}'_{3-y}$, $\text{Si}(\text{O-SiR}'_2)\text{OR}'$, R'' , Li , AlR'_2 , Hg-X , TlZ_2
 and Mg-X ,

y is an integer equal to or less than 3,
 R' is alkyl, aryl, cycloalkyl, aralkyl or
 10 cycloaryl,

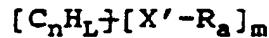
X is a halide,

X' is a polynuclear aromatic, polyheteronuclear
 aromatic or metallocopolyheteronuclear aromatic moiety,

15 R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl
 or fluoroaralkyl, and

Z is carboxylate or trifluoroacetate.

32. A composition of matter of the formula



wherein the carbon atoms, C_n , are surface

20 carbons of a substantially cylindrical, graphitic fibril
 being substantially free of pyrolytically deposited
 carbon, the projection of the graphite layers on said
 fibrils extends for a distance of at least two fibril
 diameters,

25 n is an integer, L is a number less than 0.1n,
 m is a number less than 0.5n, a is zero or an integer
 less than 10,

each of R is selected from SO_3H , COOH , NH_2 , OH ,
 CHO , CN , COCl , halide, COSH , SH , COOR' , SR' , SiR'_3 ,
 30 $\text{Si}(\text{OR}')_y\text{R}'_{3-y}$, $\text{Si}(\text{O-SiR}'_2)\text{OR}'$, R'' , Li , AlR'_2 , Hg-X , TlZ_2
 and Mg-X ,

y is an integer equal to or less than 3,
 R' is alkyl, aryl, cycloalkyl, aralkyl or
 cycloaryl,

35 X is a halide,

X' is a polynuclear aromatic, polyheteronuclear
 aromatic or metallocopolyheteronuclear aromatic moiety,

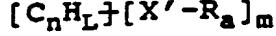
R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl
 or fluoroaralkyl, and

z is carboxylate or trifluoroacetate.

33. A composition of matter as claimed in claim 32, wherein said fibril comprises cylindrical graphitic sheets whose c-axes are substantially perpendicular to their cylindrical axis.

5 34. A composition of matter as claimed in claim 32, wherein the outer diameter of said fibrils is less than 0.1 micron.

35. A composition of matter of the formula



10 wherein the carbon atoms, C_n , are surface atoms of a fishbone fibril,

n is an integer, L is a number less than 0.1n, m is a number less than 0.5n, a is zero or an integer

15 less than 10,

each of R is selected from SO_3H , $COOH$, NH_2 , OH , CHO , CN , $COCl$, halide, $COSH$, SH , $COOR'$, SR' , SiR'_3 , $Si(O-OR')_yR'^{3-y}$, $Si(O-SiR'_2)OR'$, R'' , Li , AlR'_2 , $Hg-X$, TlZ_2 and $Mg-X$,

20 y is an integer equal to or less than 3,

R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

X is a halide,

25 X' is a polynuclear aromatic, polyheteronuclear aromatic or metallocopolyheteronuclear aromatic moiety,

R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl, and

z is carboxylate or trifluoroacetate.

36. A composition of matter of the formula



30 wherein the carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic nanotube having a length to diameter ratio of greater than 5 and a diameter of less than 0.5 micron,

35 n is an integer, L is a number less than 0.1n, m is a number less than 0.5n, a is an integer less than 10,

each of A is selected from



5 Y is an appropriate functional group of a protein, a peptide, an enzyme, an antibody, a nucleotide, an oligonucleotide, an antigen, or an enzyme substrate,

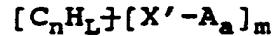
10 enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from $\text{R}'-\text{OH}$, $\text{R}'-\text{NH}_2$, $\text{R}'\text{SH}$, $\text{R}'\text{CHO}$, $\text{R}'\text{CN}$, $\text{R}'\text{X}$, $\text{R}'\text{SiR}'_3$, $\text{R}'\text{Si}(\text{OR}')_y\text{R}'_3-y$, $\text{R}'\text{Si}(\text{O}-\text{SiR}'_2)\text{OR}'$, $\text{R}'-\text{R}''$, $\text{R}'-\text{N}-\text{CO}$, $(\text{C}_2\text{H}_4\text{O})_w\text{H}$, $(\text{C}_3\text{H}_6\text{O})_w\text{H}$, $(\text{C}_2\text{H}_4\text{O})_w-\text{R}'$, $(\text{C}_3\text{H}_6\text{O})_w-\text{R}'$ and R' ,

15 y is an integer equal to or less than 3,
 R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,
 R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

20 X is a halide,
 X' is a polynuclear aromatic, polyheteronuclear aromatic or metallocopolyheteronuclear aromatic moiety,
 Z is carboxylate or trifluoroacetate, and
 w is an integer greater than one and less than

25 200.

37. A composition of matter of the formula



wherein the carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic fibril

30 being substantially free of pyrolytically deposited carbon, the projection of the graphite layers on said fibrils extends for a distance of at least two fibril diameters,

n is an integer, L is a number less than 0.1n,
35 m is a number less than 0.5n, a is an integer less than 10,

each of A is selected from



40

Y is an appropriate functional group of a protein, a peptide, an enzyme, an antibody, a nucleotide, an oligonucleotide, an antigen, or an enzyme substrate, enzyme inhibitor or the transition state analog of an 5 enzyme substrate or is selected from R'-OH, R'-NH₂, R'-SH, R'CHO, R'CN, R'X, R'SiR'₃, R'Si~~O~~R'_yR'_{3-y}, R'Si~~O~~-SiR'₂~~O~~R', R'-R'', R'-N-CO, (C₂H₄O)_wH, (C₃H₆O)_wH, (C₂H₄O)_w-R', (C₃H₆O)_w-R' and R',

Y is an integer equal to or less than 3,
10 R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,
R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

X is a halide,
15 X' is a polynuclear aromatic, polyheteronuclear aromatic or metallocopolyheteronuclear aromatic moiety,
Z is carboxylate or trifluoroacetate, and
w is an integer greater than one and less than 200.

20 38. A composition of matter as claimed in claim 37, wherein said fibril comprises cylindrical graphitic sheets whose c-axes are substantially perpendicular to their cylindrical axis.

25 39. A composition of matter as claimed in claim 37, wherein the outer diameter of said fibrils is less than 0.1 micron.

40. A composition of matter of the formula
[C_nH_L]_m[X'-A_a]_m
wherein the carbon atoms, C_n, are surface atoms
30 of a fishbone fibril,

n is an integer, L is a number less than 0.1n, m is a number less than 0.5n, a is an integer less than 10,

each of A is selected from
35 O O O O
| | | |
OY, NHY, C-OY, C-NR'Y, C-SY, C-Y, -CR'₂-OY, N=Y, and C=Y,
Y is an appropriate functional group of a
40 protein, a peptide, an enzyme, an antibody, a nucleotide, an oligonucleotide, an antigen, or an enzyme substrate,

enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from R'-OH, R'-NH₂, R'SH, R'CHO, R'CN, R'X, R'SiR'₃, R'Si{OR'}_yR'_{3-y}, R'Si{O-SiR'₂}OR', R'-R'', R'-N-CO, (C₂H₄O)_wH, (C₃H₆O)_wH, (C₂H₄O)_w-

5 R', (C₃H₆O)_w-R' and R',

y is an integer equal to or less than 3,

R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

10 R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

X is a halide,

X' is a polynuclear aromatic, polyheteronuclear aromatic or metallocopolyheteronuclear aromatic moiety,

Z is carboxylate or trifluoroacetate, and

15 w is an integer greater than one and less than 200.

41. A composition of matter as claimed in claims 31-40, wherein X' is a phthalocyanine or porphyrin.

20 42. A method of forming a composition of matter of the formula



wherein the carbon atoms, C_n, are surface carbons of a substantially cylindrical, graphitic 25 nanotube,

n is an integer, L is a number less than 0.1n, m is a number less than 0.5n,

each of R is the same and is selected from SO₃H, COOH, NH₂, OH, CHO, CN, COCl, halide, COSH, SH, 30 COOR', SR', SiR'₃, Si{OR'}_yR'_{3-y}, Si{O-SiR'₂}OR', R'', Li, AlR'₂, Hg-X, TlZ₂ and Mg-X, y is an integer equal to or less than 3,

R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

35 R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

X is a halide, and

Z is carboxylate or trifluoroacetate,

comprising the step of reacting the surface carbons with an appropriate reagent under conditions sufficient to form functionalized nanotubes having the formula $[C_nH_L]_xR_m$.

5 43. A method of forming a composition of matter of the formula



wherein the carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic 10 nanotube,

n is an integer, L is a number less than 0.1n and m is a number less than 0.5n,

each of R is selected from SO_3H , $COOH$, NH_2 , OH , CHO , CN , $COCl$, halide, $COSH$, SH , $COOR'$, SR' , SiR'_3 , 15 $Si\{OR'\}_yR''_{3-y}$, $Si\{O-SiR'_2\}OR'$, R'' , Li , AlR'_2 , $Hg-X$, TlZ_2 and $Mg-X$,

y is an integer equal to or less than 3,

R' is selected from alkyl, aryl, cycloalkyl, aralkyl, cycloaryl,

20 R'' is a fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

X is a halide,

Z is carboxylate or trifluoroacetate,

and further provided that where each of R is an 25 oxygen-containing group $COOH$ is not present,

comprising the step of reacting the surface carbons with at least one appropriate reagent under conditions sufficient to form functionalized nanotubes having the formula $[C_nH_L]_xR_m$.

30 44. A method of forming a composition of matter of the formula



wherein the carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic 35 nanotube,

n is an integer, L is a number less than 0.1n and m is a number less than 0.5n,

each of R is selected from SO_3H , $COOH$, NH_2 , OH , CHO , CN , $COCl$, halide, $COSH$, SH , $COOR'$, SR' , SiR'_3 ,

$\text{Si-OR}'_y\text{R}'_{3-y}$, $\text{Si-O-SiR}'_2\text{OR}'$, R'' , Li , AlR'_2 , Hg-X , TlZ_2 and Mg-X ,

y is an integer equal to or less than 3,
 R' is selected from alkyl, aryl, cycloalkyl,

5 aralkyl, cycloaryl,

R'' is a fluoroalkyl, fluoroaryl,
 fluorocycloalkyl or fluoroaralkyl,

X is a halide,

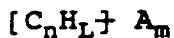
Z is carboxylate or trifluoroacetate,

10 and further provided that each of R does not contain oxygen,

comprising the step of reacting the surface carbons with at least one appropriate reagent under conditions sufficient to form functionalized nanotubes

15 having the formula $[\text{C}_n\text{H}_L]^{\text{R}_m}$.

45. A method of forming a composition of matter of the formula



wherein the carbon atoms, C_n , are surface 20 carbons of a substantially cylindrical, graphitic nanotube,

n is an integer, L is a number less than $0.1n$,
 m is a number less than $0.5n$,

each of A is selected from

25



$\text{C}=\text{Y}$,

30

Y is an appropriate functional group of a

protein, a peptide, an enzyme, an antibody, an oligonucleotide, a nucleotide, an antigen, or an enzyme substrate, enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from $\text{R}'\text{-OH}$,

35 $\text{R}'\text{-NH}_2$, $\text{R}'\text{SH}$, $\text{R}'\text{CHO}$, $\text{R}'\text{CN}$, $\text{R}'\text{X}$, $\text{R}'\text{SiR}'_3$, $\text{R}'\text{-R}''$, $\text{R}'\text{-N-}$
 CO , $(\text{C}_2\text{H}_4\text{O})_w\text{H}$, $(\text{C}_3\text{H}_6\text{O})_w\text{H}$, $(\text{C}_2\text{H}_4\text{O})_w\text{-R}'$, $(\text{C}_3\text{H}_6\text{O})_w\text{-R}'$ and R' ,

R' is alkyl, aryl, cycloalkyl, aralkyl or

cycloaryl,

R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl

40 or fluoroaralkyl,

X is a halide,

200, Z is carboxylate or trifluoroacetate, and w is an integer greater than one and less than

200,

comprising the steps of:

5 (a) reacting the surface carbons with at least one appropriate reagent under conditions sufficient to form substituted nanotubes having the formula $[C_nH_L]R_m$, wherein each of R is the same and is selected from SO_3H , $COOH$, NH_2 , OH , CHO , CN , $COCl$, halide, $COSH$, SH , $COOR'$, SR' , $Si\{OR'\}_yR'^{3-y}$, $Si\{O-SiR'\}_2OR'$, R'' , Li , AlR'^2 , $Hg-X$, TlZ_2 and $Mg-X$, and y is an integer equal to or less than 3; and

10 (b) reacting the substituted nanotubes $[C_nH_L]R_m$ with at least one appropriate reagent under conditions sufficient to form functionalized nanotubes having the formula $[C_nH_L]A_m$.

20 46. A method of forming a composition of matter of the formula



25 wherein the carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic nanotube having a length to diameter ratio of greater than 5 and a diameter of less than 0.1 micron, n is an integer, L is a number less than 0.1n, m is a number less than 0.5n, each of A is selected from

30 O O O O
 $|$ $|$ $|$ $|$
 OY , NHY , $C-OY$, $C-NR'Y$, $C-SY$, $C-Y$, $-CR'^2-OY$, $N=Y$, and $C=Y$,

35 Y is an appropriate functional group of a protein, a peptide, an enzyme, an antibody, an oligonucleotide, a nucleotide, an antigen, or an enzyme substrate, enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from $R'-OH$, $R'-NH_2$, $R'SH$, $R'CHO$, $R'CN$, $R'X$, $R'SiR'^3$, $R'-R''$, $R'-N-CO$, $(C_2H_4O)_wH$, $(C_3H_6O)_wH$, $(C_2H_4O)_w-R'$, $(C_3H_6O)_w-R'$ and R' ,

R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

R" is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

5 X is a halide,

Z is carboxylate or trifluoroacetate, and

w is an integer greater than one and less than 200,

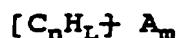
comprising the steps of:

10 (a) reacting the surface carbons with at least one appropriate reagent under conditions sufficient to form substituted nanotubes having the formula $[C_nH_L]R_m$, wherein each of R is selected from SO_3H , $COOH$, NH_2 , OH , CHO , CN , $COCl$, halide, $COSH$, SH , $COOR'$, SR' , SiR'_3 , $Si(OR')_yR'^{3-y}$, $Si(O-SiR'_2)OR'$,

15 R'' , Li , AlR'_2 , $Hg-X$, TlZ_2 and $Mg-X$, and y is an integer equal to or less than 3; and

(b) reacting the substituted nanotubes $[C_nH_L]R_m$ with at least one appropriate reagent under conditions sufficient to form functionalized nanotubes having the formula $[C_nH_L]A_m$.

20 47. A method of forming a composition of matter of the formula



25 wherein the carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic nanotube being substantially free of pyrolytically deposited carbon,

30 n is an integer, L is a number less than 0.1n,

m is a number less than 0.5n,

each of A is selected from

35 OY , NHY , $C-OY$, $C-NR'Y$, $C-SY$, $C-Y$, $-CR'_2-OY$, $N=Y$, and $C=Y$,

40 Y is an appropriate functional group of a protein, a peptide, an enzyme, an antibody, an oligonucleotide, a nucleotide, an antigen, or an enzyme

substrate, enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from $R'-OH$, $R'-NH_2$, $R'SH$, $R'CHO$, $R'CN$, $R'X$, $R'SiR'_3$, $R'-R''$, $R'-N-CO$, $(C_2H_4O)_wH$, $(C_3H_6O)_wH$, $(C_2H_4O)_w-R'$, $(C_3H_6O)_w-R'$ and R' ,

5 R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluorocaralkyl,

X is a halide,

10 Z is carboxylate or trifluoroacetate, and

w is an integer greater than one and less than 200,

comprising the steps of:

15 (a) reacting the surface carbons with at least one appropriate reagent under conditions sufficient to form substituted nanotubes having the formula $[C_nH_L]^R_m$, wherein each of R is selected from SO_3H , $COOH$, NH_2 , OH , CHO , CN , $COCl$, halide, $COSH$, SH , $COOR'$,
20 SR' , SiR'_3 , $Si\{OR'\}_yR'^{3-y}$, $Si\{O-SiR'_2\}OR'$, R'' , Li , AlR'_2 , $Hg-X$, TlZ_2 and $Mg-X$, and y is an integer equal to or less than 3; and
(b) reacting the substituted nanotubes $[C_nH_L]^R_m$ with at least one appropriate reagent
25 under conditions sufficient to form functionalized nanotubes having the formula $[C_nH_L]^A_m$.

48. A method of forming a composition of matter of the formula

30 $[C_nH_L]^A_m$

wherein the carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic nanotube,

n is an integer, L is a number less than 0.1n,

35 m is a number less than 0.5n,

each of A is selected from



5 OY, NHY, C-OY, C-NR'Y, C-SY, C-Y, -CR'₂-OY, N=Y, and C=Y,

Y is an appropriate functional group of a protein, a peptide, an enzyme, an antibody, an 10 oligonucleotide, a nucleotide, an antigen, or an enzyme substrate, enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from R'-OH, R'-NH₂, R'SH, R'CHO, R'CN, R'X, R'SiR'₃, R"-R", R'-N-CO, (C₂H₄O)_wH, (C₃H₆O)_wH, (C₂H₄O)_w-R', (C₃H₆O)_w-R' and R', 15 R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

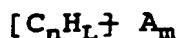
R" is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

X is a halide,

20 Z is carboxylate or trifluoroacetate, and w is an integer greater than one and less than 200,

comprising the step of reacting substituted nanotubes [C_nH_L]_R_m with at least one appropriate reagent 25 under conditions sufficient to form functionalized nanotubes having the formula [C_nH_L]_A_m, where each of R is the same and is selected from SO₃H, COOH, NH₂, OH, CHO, CN, COCl, halide, COSH, SH, COOR', SR', SiR'₃, Si(OR')_yR'_{3-y}, Si(O-SiR'₂)OR', R", Li, AlR'₂, Hg-X, TlZ₂ 30 and Mg-X, and y is an integer equal to or less than 3.

49. A method of forming a composition of matter of the formula

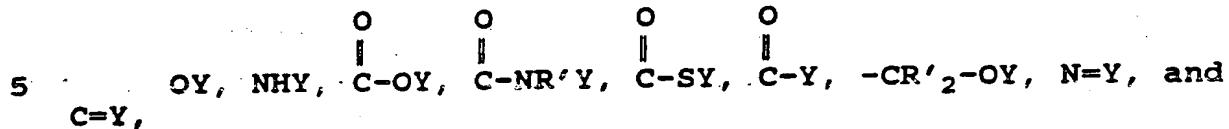


wherein the carbon atoms, C_n, are surface 35 carbons of a substantially cylindrical, graphitic nanotube having a length to diameter ratio of greater than 5 and a diameter of less than 0.1 micron,

n is an integer, L is a number less than 0.1n,

m is a number less than 0.5n,

each of A is selected from



Y is an appropriate functional group of a protein, a peptide, an enzyme, an antibody, an oligonucleotide, a nucleotide, an antigen, or an enzyme substrate, enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from $R''-OH$, $R''-NH_2$, $R''SH$, $R''CHO$, $R''CN$, $R''X$, $R''SiR''_3$, $R''-R''$, $R''-N-CO$, $(C_2H_4O)_wH$, $(C_3H_6O)_wH$, $(C_2H_4O)_w-R'$, $(C_3H_6O)_w-R'$ and R' ,
 15 R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

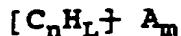
R" is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl.

x is a halide,

20 z is carboxylate or trifluoroacetate, and
w is an integer greater than one and less than
200,

comprising the step of reacting substituted nanotubes $[C_nH_L]R_m$ with at least one appropriate reagent under conditions sufficient to form functionalized nanotubes having the formula $[C_nH_L]A_m$, where each of R is selected from SO_3H , $COOH$, NH_2 , OH , CHO , CN , $COCl$, halide, $COSH$, SH , $COOR'$, SR' , SiR'_3 , $Si\{OR'\}_yR'^{3-y}$, $Si\{O-SiR'_2\}OR'$, R'' , Li , AlR'_2 , $Hg-X$, TlZ_2 and $Mg-X$, and y is an integer equal to or less than 3.

50. A method of forming a composition of matter of the formula



wherein the carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic nanotube being substantially free of pyrolytically deposited carbon,

n is an integer, L is a number less than 0.1n,
m is a number less than 0.5n,

each of A is selected from

5 $\begin{array}{c} \text{O} \\ | \\ \text{OY} \end{array}$, NHY , $\begin{array}{c} \text{O} \\ | \\ \text{C-OY} \end{array}$, $\begin{array}{c} \text{O} \\ | \\ \text{C-NR'Y} \end{array}$, $\begin{array}{c} \text{O} \\ | \\ \text{C-SY} \end{array}$, $\begin{array}{c} \text{O} \\ | \\ \text{C-Y} \end{array}$, $-\text{CR'}_2\text{-OY}$, N=Y , and
 C=Y ,

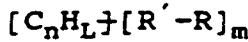
Y is an appropriate functional group of a protein, a peptide, an enzyme, an antibody, an 10 oligonucleotide, a nucleotide, an antigen, or an enzyme substrate, enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from $\text{R}'\text{-OH}$, $\text{R}'\text{-NH}_2$, $\text{R}'\text{SH}$, $\text{R}'\text{CHO}$, $\text{R}'\text{CN}$, $\text{R}'\text{X}$, $\text{R}'\text{SiR'}_3$, $\text{R}'\text{-R''}$, $\text{R}'\text{-N-CO}$, $(\text{C}_2\text{H}_4\text{O})_w\text{H}$, $\text{C}_3\text{H}_6\text{O}_w\text{H}$, $(\text{C}_2\text{H}_4\text{O})_w\text{-R'}$, $(\text{C}_3\text{H}_6\text{O})_w\text{-R'}$ and R' ,
15 R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

20 X is a halide,
 Z is carboxylate or trifluoroacetate, and
w is an integer greater than one and less than 200,

comprising the step of reacting substituted 25 nanotubes $[\text{C}_n\text{H}_L]^{\text{+}}\text{R}_m$ with at least one appropriate reagent under conditions sufficient to form functionalized nanotubes having the formula $[\text{C}_n\text{H}_L]^{\text{+}}\text{A}_m$, where each of R is selected from SO_3H , COOH , NH_2 , OH , CHO , CN , COCl , halide, COSH , SH , COOR' , SR' , SiR'_3 , $\text{Si}(\text{OR}')_y\text{R}'_{3-y}$, $\text{Si}(\text{O-})$
30 $\text{SiR'}_2\text{OR}'$, R'' , Li , AlR'_2 , Hg-X , TlZ_2 and Mg-X , and y is an integer equal to or less than 3.

51. A method of forming a composition of matter of the formula



wherein the carbon atoms, C_n , are surface 35 carbons of a substantially cylindrical, graphitic nanotube,

n is an integer, L is a number less than 0.1n, m is a number less than 0.5n,
each of R is selected from SO_3H , COOH , NH_2 , OH ,
40 CHO , CN , COCl , halide, COSH , SH , COOR' , SR' , SiR'_3 ,

$\text{Si}(\text{OR}')_y\text{R}'_{3-y}$, $\text{Si}(\text{O-SiR}'_2)\text{OR}'$, R'' , Li , AlR'_2 , Hg-X , TlZ_2 and Mg-X ,

y is an integer equal to or less than 3,

R' is alkyl, aryl, cycloalkyl, aralkyl or

5 cycloaryl,

X is a halide,

R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl, and

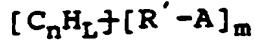
Z is carboxylate or trifluoroacetate,

10 comprising the steps of:

(a) deoxygenating the graphitic nanotubes under conditions sufficient to form deoxygenated nanotubes; and

(b) reacting the deoxygenated nanotubes with 15 at least one appropriate activated olefin under conditions sufficient to form functionalized nanotubes having the formula $[\text{C}_n\text{H}_L][\text{R}'-\text{R}]_m$.

52. A method of forming a composition of 20 matter of the formula



wherein the carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic nanotube,

25 n is an integer, L is a number less than 0.1n,

m is a number less than 0.5n,

R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

X is a halide,

30 each of A is selected from



Y is an appropriate functional group of a

35 protein, a peptide, an enzyme, an antibody, an oligonucleotide, a nucleotide, an antigen, or an enzyme substrate, enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from $\text{R}'\text{-OH}$, $\text{R}'\text{-NH}_2$, $\text{R}'\text{SH}$, $\text{R}'\text{CHO}$, $\text{R}'\text{CN}$, $\text{R}'\text{X}$, $\text{R}'\text{SiR}'_3$, $\text{R}'\text{-R}''$, $\text{R}'\text{-N-CO}$, $(\text{C}_2\text{H}_4\text{O})_w\text{H}$, $(\text{C}_3\text{H}_6\text{O})_w\text{H}$, $(\text{C}_2\text{H}_4\text{O})_w\text{-R}'$, $(\text{C}_3\text{H}_6\text{O})_w\text{-R}'$ and R' ,

R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl, and

Z is carboxylate or trifluoroacetate, comprising the steps of:

5 (a) deoxygenating the graphitic nanotubes under conditions sufficient to form deoxygenated nanotubes;

10 (b) reacting the deoxygenated nanotubes with at least one appropriate activated olefin to form substituted nanotubes having the formula $[C_nH_L][R'-R]_m$, where each of R is selected from SO_3H , $COOH$, NH_2 , OH , CHO , CN , $COCl$, halide, $COSH$, SH , $COOR'$, SR' , SiR'_3 , $Si\{OR'\}_yR'^{3-y}$,

15 $Si\{O-SiR'_2\}OR'$, R'' , Li , AlR'_2 , $Hg-X$, TlZ_2 and $Mg-X$, and y is an integer equal to or less than 3; and

20 (c) reacting the substituted nanotubes having the formula $[C_nH_L][R'-R]_m$ with at least one appropriate reagent under conditions sufficient to form functionalized nanotubes having the formula $[C_nH_L][R'-A]_m$.

53. A method of forming a composition of matter of the formula

25 $[C_nH_L][R'-A]_m$

wherein the carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic nanotube,

n is an integer, L is a number less than 0.1n,

30 m is a number less than 0.5n,

R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

X is a halide,

each of A is selected from

35

O O O O
| | | |
 OY , NHY , $C-OY$, $C-NR'Y$, $C-SY$, $C-Y$, $-CR'_2-OY$, $N=Y$, and $C=Y$,

Y is an appropriate functional group of a

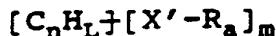
protein, a peptide, an enzyme, an antibody, an

40 oligonucleotide, a nucleotide, an antigen, or an enzyme

substrate, enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from $R'-OH$, $R'-NH_2$, $R'SH$, $R'CHO$, $R'CN$, $R'X$, $R'SiR'_3$, $R'-R''$, $R'-N-CO$, $(C_2H_4O)_wH$, $(C_3H_6O)_wH$, $(C_2H_4O)_w-R'$, $(C_3H_6O)_w-R'$ and R' ,
5 R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl, and

Z is carboxylate or trifluoroacetate, comprising the step of reacting substituted nanotubes having the formula $[C_nH_L][R'-R]_m$ with at least 10 one appropriate reagent under conditions sufficient to form functionalized nanotubes having the formula $[C_nH_L][R'-A]_m$, where each of R is selected from SO_3H , $COOH$, NH_2 , OH , CHO , CN , $COCl$, halide, $COSH$, SH , $COOR'$, SR' , SiR'_3 , $Si(OR')_yR'^{3-y}$, $Si(O-SiR'_2)OR'$, R'' , Li , AlR'_2 , 15 $Hg-X$, TlZ_2 and $Mg-X$, and y is an integer equal to or less than 3.

54. A method of forming a composition of matter of the formula



20 wherein the carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic nanotube,

n is an integer, L is a number less than 0.1n, 25 m is a number less than 0.5n, a is zero or an integer less than 10,

each of R is selected from SO_3H , $COOH$, NH_2 , OH , CHO , CN , $COCl$, halide, $COSH$, SH , $COOR'$, SR' , SiR'_3 , $Si(OR')_yR'^{3-y}$, $Si(O-SiR'_2)OR'$, R'' , Li , AlR'_2 , $Hg-X$, TlZ_2 and $Mg-X$,

30 y is an integer equal to or less than 3, R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

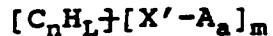
X is a halide,

35 X' is a polynuclear aromatic, polyheteronuclear aromatic or metallocopolyheteronuclear aromatic moiety, R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl, and

Z is carboxylate or trifluoroacetate,

comprising the step of adsorbing at least one appropriate macrocyclic compound onto the surface of the graphitic nanotube under conditions sufficient to form a functionalized nanotube having the formula $[C_nH_L][X'-R_a]_m$.

5 55. A method of forming a composition of matter of the formula



wherein the carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic 10 nanotube,

n is an integer, L is a number less than $0.1n$, m is a number less than $0.5n$, a is an integer less than 10,

each of A is selected from

15
$$\begin{array}{c} O & O & O & O \\ | & | & | & | \\ OY, \text{ NHY, } C-OY, \text{ C-NR}'Y, \text{ C-SY, } C-Y, \text{ -CR}'_2-OY, \text{ N=Y, and } C=Y, \end{array}$$

Y is an appropriate functional group of a 20 protein, a peptide, an enzyme, an antibody, an oligonucleotide, a nucleotide, an antigen, or an enzyme substrate, enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from $R'-OH$, $R'-NH_2$, $R'SH$, $R'CHO$, $R'CN$, $R'X$, $R'SiR'_3$, $R'-R''$, $R'-N-CO$, 25 $(C_2H_4O)_wH$, $(C_3H_6O)_wH$, $(C_2H_4O)_w-R'$, $(C_3H_6O)_w-R'$ and R' , R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

X is a halide,

30 X' is a polynuclear aromatic, polyheteronuclear aromatic or metallocopolyheteronuclear aromatic moiety,

Z is carboxylate or trifluoroacetate, and

w is an integer greater than one and less than 200,

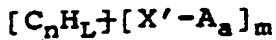
35 comprising the steps of:

(a) adsorbing at least one appropriate macrocyclic compound onto the surface of the graphitic nanotube under conditions sufficient to form a substituted nanotube having the formula $[C_nH_L][X'-R_a]_m$, where each of R is selected from SO_3H , $COOH$, NH_2 ,

OH, CHO, CN, COCl, halide, COSH, SH, COOR', SR', SiR'₃, Si⁺OR'_yR'_{3-y}, Si⁺O-SiR'₂OR', R'', Li, AlR'₂, Hg-X, TlZ₂ and Mg-X, and y is an integer equal to or less than 3; and

5 (b) reacting the substituted nanotubes [C_nH_L]⁺[X'-R_a]_m with at least one appropriate reagent under conditions sufficient to form a functionalized 10 nanotube having the formula [C_nH_L]⁺[X'-A_a]_m.

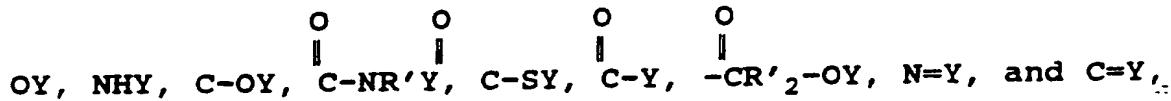
56. A method of forming a composition of matter of the formula



wherein the carbon atoms, C_n, are surface 15 carbons of a substantially cylindrical, graphitic nanotube,

wherein n is an integer, L is a number less than 0.1n, m is a number less than 0.5n, a is an integer less than 10,

20 each of A is selected from



25 Y is an appropriate functional group of a protein, a peptide, an enzyme, an antibody, an oligonucleotide, a nucleotide, an antigen, or an enzyme substrate, enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from R'-OH, 30 R'-NH₂, R'SH, R'CHO, R'CN, R'X, R'SiR'₃, R'-R'', R'-N-CO, (C₂H₄O)_wH, (C₃H₆O)_wH, (C₂H₄O)_w-R', (C₃H₆O)_w-R' and R', R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

35 R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

X is a halide,

X' is a polynuclear aromatic, polyheteronuclear aromatic or metallocopolyheteronuclear aromatic moiety,

Z is carboxylate or trifluoroacetate, and

40 w is an integer greater than one and less than

comprising the step of reacting the substituted nanotubes $[C_nH_L][X'-R_a]_m$ with at least one appropriate reagent under conditions sufficient to form a functionalized nanotube having the formula $[C_nH_L][X'-A_a]_m$,
5 where each of R is selected from SO_3H , $COOH$, NH_2 , OH , CHO , CN , $COCl$, halide, $COSH$, SH , $COOR'$, SR' , SiR'_3 , $Si\{OR'\}_yR'^{3-y}$, $Si\{O-SiR'_2\}OR'$, R'' , Li , AlR'_2 , $Hg-X$, TlZ_2 and $Mg-X$, and y is an integer equal to or less than 3.

57. A method as recited in claims 54 or 55,
10 wherein prior to the step of adsorbing onto the surface carbons, the graphitic nanotubes are dispersed in a medium.

58. A method as recited in claims 42, 43, 44, 45, 46 or 47, wherein prior to the step of reacting the 15 surface carbons, the graphitic nanotubes are dispersed in a medium.

59. A method as recited in claims 45, 46, 47, 48, 49, 50, 52, 53, 55 or 56, wherein prior to the step 20 of reacting the substituted nanotubes with the reagent, the substituted nanotubes are dispersed in a medium.

60. A method as recited in claims 42, 43, 44, 45, 46 or 47, wherein the step of reacting the surface carbons comprises sulfonating the surface carbons.

61. A method as recited in claims 42, 43, 44, 25 45, 46, 47, 48, 49 or 50, wherein the step of reacting the surface carbons comprises metallizing the surface carbons with an organometallic reagent.

62. The method as recited in claims 47 or 50, wherein the projection of the graphite layers on said 30 nanotubes extends for a distance of at least two nanotube diameters.

63. The method as recited in claims 47 or 50, wherein said nanotube comprises cylindrical graphitic sheets whose c-axes are substantially perpendicular to 35 their cylindrical axis.

64. The method as recited in claims 47 or 50, wherein the outer diameter of said nanotubes is less than 0.1. micron.

65. The method as recited in claims 47 or 50, wherein the carbon atoms, C_n , are surface atoms of a fishbone fibril.

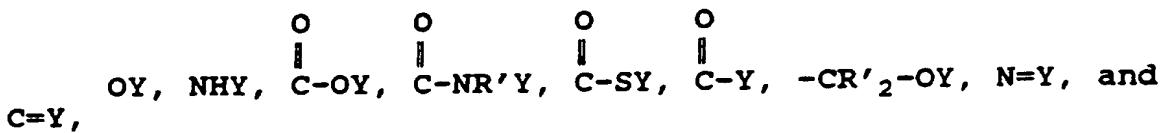
66. A method of introducing functional groups onto the surface of carbon nanotubes to form a functionalized nanotube having the formula



wherein the carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic nanotube being substantially free of pyrolytically deposited carbon,

n is an integer, L is a number less than 0.1n, m is a number less than 0.5n,

each of A is selected from



Y is an appropriate functional group of a protein, a peptide, an enzyme, an antibody, an oligonucleotide, a nucleotide, an antigen, or an enzyme substrate, enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from $R'-OH$, $R'-NH_2$, $R'SH$, $R'CHO$, $R'CN$, $R'X$, $R'SiR'_3$, $R'-R''$, $R'-N-CO$, $(C_2H_4O)_wH$, $(C_3H_6O)_wH$, $(C_2H_4O)_w-R'$, $(C_3H_6O)_w-R'$ and R' , R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

X is a halide,

Z is carboxylate or trifluoroacetate, and

w is an integer greater than one and less than

35 200,

comprising the steps of:

- (a) contacting the carbon fibrils with oxidizing agents selected from the group including a solution of an alkali metal chlorate in a strong acid for a period of time sufficient

to oxidize the surface of said fibrils; and

5 (b) contacting the surface-oxidized carbon fibrils with reactant suitable for adding a functional group to the surface of the carbon fibrils.

67. A method as recited in claim 66, wherein the carbon fibrils are subjected to processing prior to contact with the oxidizing agents.

10 68. A method as recited in claim 66, wherein the processing comprises dispersing the carbon fibrils in a solvent.

15 69. A method as recited in claim 68, wherein after being dispersed in the solvent the carbon fibrils are filtered and dried.

70. A method as recited in claim 66, wherein the alkali metal chlorate is sodium chlorate or potassium chlorate.

71. A method as recited in claim 66, wherein 20 the strong acid is sulfuric acid.

72. A method as recited in claim 66, wherein the functional group added to the surface-oxidized fibrils is alkyl/aryl silane.

73. A method as recited in claim 66, wherein 25 the functional group added to the surface-oxidized fibrils is a long chain alkyl/aralkyl group.

74. A method as recited in claim 66, wherein the functional group added to the surface-oxidized fibrils is a long chain hydroxyl group.

75. A method as recited in claim 66, wherein 30 the functional group added to the surface-oxidized fibrils is a long chain amine group.

76. A method as recited in claim 66, wherein 35 the functional group added to the surface-oxidized fibrils is a fluorocarbon.

77. A method as recited in claim 66, wherein the time sufficient for oxidization is between about 0.5 hour and 24 hours.

78. A network of functionalized fibrils comprising at least two functionalized fibrils linked at functional groups by either one or more direct bonds or at least one linker moiety, wherein said linker moiety is 5 either bifunctional or polyfunctional.

79. A composition of matter of the formula

$$[F.F. + \text{linker} + F.F.]$$

 wherein the linker is a bifunctional or polyfunctional moiety linked to an appropriate 10 functionalized fibril, [F.F.], derived from the following substituted fibrils:

- (i) $[C_nH_L]^nR_m;$
- (ii) $[C_nH_L]^nR_m;$
- (iii) $[C_nH_L]^nA_m;$
- 15 (iv) $[C_nH_L]^n[R'-R]_m;$
- (v) $[C_nH_L]^n[R'-A]_m;$
- (vi) $[C_nH_L]^n[X'-R_a]_m;$ and
- (vii) $[C_nH_L]^n[X'-A_a]_m;$

where the carbon atoms, C_n , are surface carbons 20 of a graphitic nanotube,

n is an integer, L is a number less than 0.1n and m is a number less than 0.5n, a is zero or an integer less than 10,

each of R is selected from SO_3H , $COOH$, NH_2 , OH , 25 CHO , CN , $COCl$, halide, $COSH$, SH , $COOR'$, SR' , SiR'_3 , $Si\{OR'\}_yR''_{3-y}$, $Si\{O-SiR'_2\}OR'$, R'' , Li , AlR''_2 , $Hg-X$, TlZ_2 and $Mg-X$,

y is an integer equal to or less than 3,
 A is selected from

30 $O \quad O \quad O \quad O$
 $|| \quad || \quad || \quad ||$
 $OY, NHY, C-OY, C-NR'Y, C-SY, C-Y, -CR''_2-OY, N=Y, \text{ and } C=Y,$

Y is an appropriate functional group of a 35 protein, a peptide, an enzyme, an antibody, an oligonucleotide, a nucleotide, an antigen, or an enzyme substrate, enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from $R'-OH$, $R'-NH_2$, $R'SH$, $R'CHO$, $R'CN$, $R'X$, $R'SiR'_3$, $R'-R''$, $R'-N-CO$, 40 $(C_2H_4O)_wH$, $(C_3H_6O)_wH$, $(C_2H_4O)_w-R'$, $(C_3H_6O)_w-R'$ and R' ,

R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

R" is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

5 X is a halide,

X' is a polynuclear aromatic, polyheteronuclear aromatic or metallopolyheteronuclear aromatic moiety,

Z is carboxylate or trifluoroacetate, and

w is an integer greater than one and less than

10 200.

80. A method for producing a network of carbon fibrils comprising contacting carbon fibrils with a strong oxidizing agent for a period of time sufficient to oxidize the surface of said carbon fibrils; contacting 15 said surface-oxidized fibrils with reactant suitable for adding a functional group to the surface of the carbon fibrils; and further contacting said surface-functionalized fibrils with an amount of a cross-linking agent effective for producing a network of carbon 20 fibrils.

81. A method for producing a network of carbon fibrils comprising the steps of:

(a) contacting the fibrils with a 25 solution of an alkali metal chlorate in a strong acid for a period of time sufficient to oxidize the surface of said fibrils;

(b) contacting the surface-oxidized fibrils with a reactant suitable for adding a functional group to the surface of the carbon fibrils; and

(c) further contacting said 30 functionalized fibrils with an effective amount of a cross-linking agent.

82. A method as recited in claims 81 or 82, wherein the cross-linking agent is a diol or diamine.

83. A method for producing a network of carbon fibrils comprising contacting carbon fibrils with a

strong oxidizing agent for a period of time sufficient to oxidize the surface of said carbon fibrils and contacting said surface-oxidized fibrils with an amount of a cross-linking agent effective for producing a network of carbon 5 fibrils.

84. A method as recited in claim 83, wherein the strong oxidizing agent is an alkali metal chlorate or nitric acid.

85. A method as recited in claim 83, wherein 10 the cross-linking agent is a polyol or polyamine.

86. A method for producing a network of functionalized fibrils comprising reacting at least two functionalized fibrils with a linker moiety comprising a bifunctional or polyfunctional moiety.

87. A surface-functionalized carbon fibril 15 formed by the method comprising the steps of contacting carbon fibrils with an effective amount of a strong oxidizing agent for a period of time sufficient to oxidize the surface of said fibrils; and further 20 contacting said fibrils with reactant suitable for adding a functional group to the surface of said fibrils.

88. A surface-modified carbon fibril comprising a carbon fibril whose surface is uniformly substituted with a functional group.

89. A surface-modified carbon fibril as 25 claimed in claim 88, wherein the functional group is carboxyl.

90. A method of uniformly substituting the 30 surface of carbon fibrils with a functional group comprising contacting carbon fibrils with an effective amount a of reactant capable of uniformly substituting a functional group onto the surface of said carbon fibrils.

91. A method of uniformly substituting the 35 surface of carbon fibrils with a functional group as claimed in claim 90, wherein the functional group is carboxyl.

92. A method as recited in claim 90, wherein the reactant is a functionalized porphyrin.

93. A method as recited in claim 90, wherein the reactant is a phthalocyanine.

94. A method as recited in claim 93, wherein the phthalocyanine is cobalt phthalocyanine.

5 95. A surface-modified carbon fibril made by the method comprising contacting carbon fibrils with an effective amount of a reactant for substituting a functional group onto the surface of said carbon fibrils.

10 96. A surface-modified carbon fibril as recited in claim 95, wherein the reactant is a functionalized porphyrin.

97. A surface-modified carbon fibril as recited in claim 96, wherein the reactant is a phthalocyanine.

15 98. A surface-modified carbon fibril as recited in claim 97, wherein the phthalocyanine is cobalt phthalocyanine.

99. A network of carbon fibrils formed by a method comprising the steps of:

20 (a) contacting carbon fibrils with an oxidizing agent for a period of time sufficient to oxidize the surface of said fibrils;

(b) contacting the surface-oxidized fibrils with reactant suitable for adding a functional group to the surface of the fibrils; and

25 (c) further contacting said surface-functionalized fibrils with an effective amount of a cross-linking agent.

30 100. An electrode comprising functionalized nanotubes.

101. An electrode as recited in claim 100, 35 wherein the functionalized nanotubes is phthalocyanine substituted nanotubes.

102. A reinforced ceramic material comprising functionalized nanotubes dispersed in a ceramic matrix material.

103. A reinforced ceramic material produced by dispersing a functionalized nanotube in an aqueous solution containing a hydrolyzable precursor of the ceramic material and converting the hydrolyzable 5 precursor to a reinforced ceramic material.

104. A method of making a reinforced ceramic material comprising dispersing a functionalized nanotube in an aqueous solution containing a hydrolyzable precursor of a ceramic matrix material and converting the 10 hydrolyzable precursor to a reinforced ceramic material.

105. A sol gel material comprising the functionalized nanotubes.

106. A porous material comprising a multiplicity of functionalized nanotube networks as 15 defined in claims 78 or 79.

107. An adsorbent material comprising the porous material of claim 103.

108. A catalyst support material comprising the porous material of claim 103.

20 109. A chromatography media material comprising the porous material of claim 103.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US95/16159

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :F16L 11/00; B01D 35/00; B05D 3/00; B29D 22/00

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 138/137, 177, 178; 210/500.1, 500.23, 500.27; 427/399; 428/34.1, 408, 411.1

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A,P	US, A, 5,424,054 (BETHUNE et al) 13 June 1995, see entire document.	1-109
T	ZURER, P.S. Supramolecular Chemistry Exploited To Build Nanotubes, Recognize DNA. Chemical & Engineering News January 15, 1996, pages 18-22.	1-109

Further documents are listed in the continuation of Box C. See patent family annex.

•	Special categories of cited documents:		
A	document defining the general state of the art which is not considered to be part of particular relevance	*T*	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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13 MAY 1996

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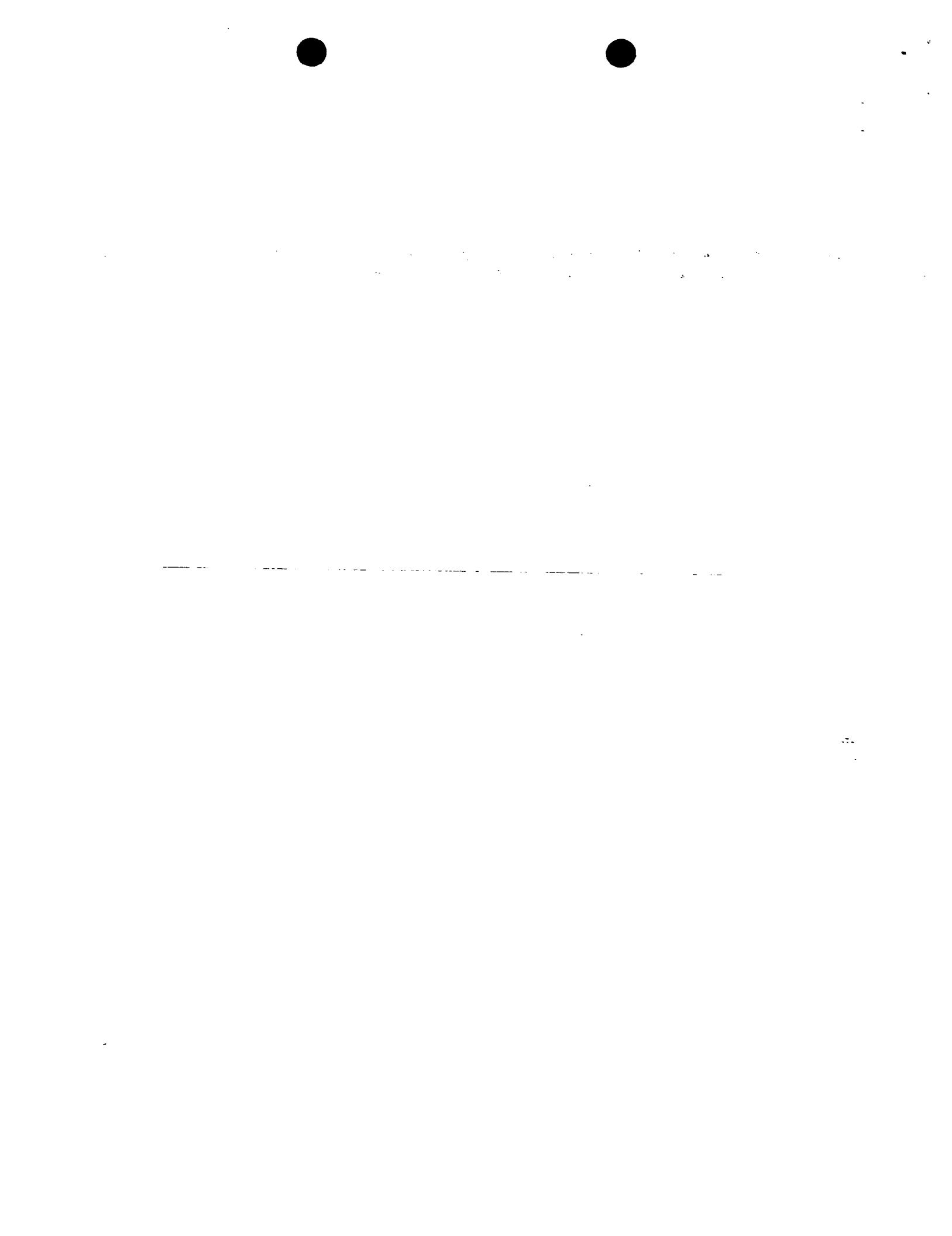
INTERNATIONAL SEARCH REPORT

International application No.

PCT/US95/16159

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

138/137, 177, 178; 210/500.1, 500.23, 500.27; 427/399; 428/34.1, 408, 411.1



**CORRECTED
VERSION***

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: **FUNCTIONALIZED FIBRILS**

(57) Abstract

Graphitic nanotubes, which includes tubular fullerenes (commonly called "buckytubes") and fibrils, which are functionalized by chemical substitution or by adsorption of functional moieties. More specifically the invention relates to graphitic nanotubes which are uniformly or non-uniformly substituted with chemical moieties or upon which certain cyclic compounds are adsorbed and to complex structures comprised of such functionalized fibrils linked to one another. The invention also relates to methods of introducing functional groups onto the surface of such fibrils.

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FUNCTIONALIZED NANOTUBES
FIELD OF THE INVENTION

The invention relates broadly to graphitic nanotubes, which includes tubular fullerenes (commonly 5 called "buckytubes") and fibrils, which are functionalized by chemical substitution or by adsorption of functional moieties. More specifically the invention relates to graphitic nanotubes which are uniformly or non-uniformly substituted with chemical moieties or upon 10 which certain cyclic compounds are adsorbed and to complex structures comprised of such functionalized fibrils linked to one another. The invention also relates to methods of introducing functional groups onto the surface of such fibrils.

15 BACKGROUND OF THE INVENTION

This invention lies in the field of submicron graphitic fibrils, sometimes called vapor grown carbon fibers. Carbon fibrils are vermicular carbon deposits having diameters less than 1.0μ , preferably less than 20 0.5μ , and even more preferably less than 0.2μ . They exist in a variety of forms and have been prepared through the catalytic decomposition of various carbon-containing gases at metal surfaces. Such vermicular carbon deposits have been observed almost since the 25 advent of electron microscopy. A good early survey and reference is found in Baker and Harris, Chemistry and Physics of Carbon, Walker and Thrower ed., Vol. 14, 1978, p. 83, hereby incorporated by reference. See also, Rodriguez, N., J. Mater. Research, Vol. 8, p. 3233 30 (1993), hereby incorporated by reference.

In 1976, Endo et al. (see Obelin, A. and Endo, M., J. of Crystal Growth, Vol. 32 (1976), pp. 335-349, hereby incorporated by reference) elucidated the basic mechanism by which such carbon fibrils grow. There were 35 seen to originate from a metal catalyst particle, which, in the presence of a hydrocarbon containing gas, becomes supersaturated in carbon. A cylindrical ordered

graphitic core is extruded which immediately, according to Endo et al., becomes coated with an outer layer of pyrolytically deposited graphite. These fibrils with a pyrolytic overcoat typically have diameters in excess of 5 0.1 μ , more typically 0.2 to 0.5 μ .

In 1983, Tennent, U.S. Patent No. 4,663,230, hereby incorporated by reference, succeeded in growing cylindrical ordered graphite cores, uncontaminated with pyrolytic carbon. Thus, the Tennent invention provided 10 access to smaller diameter fibrils, typically 35 to 700 \AA (0.0035 to 0.070 μ) and to an ordered, "as grown" graphitic surface. Fibrillar carbons of less perfect structure, but also without a pyrolytic carbon outer layer have also been grown.

15 The fibrils, buckytubes and nanofibers that are functionalized in this application are distinguishable from continuous carbon fibers commercially available as reinforcement materials. In contrast to fibrils, which have, desirably large, but unavoidably finite aspect 20 ratios, continuous carbon fibers have aspect ratios (L/D) of at least 10^4 and often 10^6 or more. The diameter of continuous fibers is also far larger than that of fibrils, being always $>1.0\mu$ and typically 5 to 7 μ .

Continuous carbon fibers are made by the 25 pyrolysis of organic precursor fibers, usually rayon, polyacrylonitrile (PAN) and pitch. Thus, they may include heteroatoms within their structure. The graphitic nature of "as made" continuous carbon fibers varies, but they may be subjected to a subsequent 30 graphitization step. Differences in degree of graphitization, orientation and crystallinity of graphite planes, if they are present, the potential presence of heteroatoms and even the absolute difference in substrate diameter make experience with continuous fibers poor 35 predictors of nanofiber chemistry.

Tennet, U.S. Patent No. 4,663,230 describes carbon fibrils that are free of a continuous thermal

carbon overcoat and have multiple graphitic outer layers that are substantially parallel to the fibril axis. As such they may be characterized as having their c-axes, the axes which are perpendicular to the tangents of the 5 curved layers of graphite, substantially perpendicular to their cylindrical axes. They generally have diameters no greater than 0.1μ and length to diameter ratios of at least 5. Desirably they are substantially free of a continuous thermal carbon overcoat, i.e., pyrolytically 10 deposited carbon resulting from thermal cracking of the gas feed used to prepare them.

Tennent, et al., US Patent No. 5,171,560, hereby incorporated by reference, describes carbon fibrils free of thermal overcoat and having graphitic 15 layers substantially parallel to the fibril axes such that the projection of said layers on said fibril axes extends for a distance of at least two fibril diameters. Typically, such fibrils are substantially cylindrical, graphitic nanotubes of substantially constant diameter 20 and comprise cylindrical graphitic sheets whose c-axes are substantially perpendicular to their cylindrical axis. They are substantially free of pyrolytically deposited carbon, have a diameter less than 0.1μ and a length to diameter ratio of greater than 5. These 25 fibrils are of primary interest in the invention.

Further details regarding the formation of carbon fibril aggregates may be found in the disclosure of Snyder et al., U.S. Patent Application Serial No. 149,573, filed January 28, 1988, and PCT Application No. 30 US89/00322, filed January 28, 1989 ("Carbon Fibrils") WO 89/07163, and Moy et al., U.S. Patent Application Serial No. 413,837 filed September 28, 1989 and PCT Application No. US90/05498, filed September 27, 1990 ("Fibril Aggregates and Method of Making Same") WO 91/05089, all 35 of which are assigned to the same assignee as the invention here and are hereby incorporated by reference.

Moy et al., USSN 07/887,307 filed May 22, 1992, hereby incorporated by reference, describes fibrils prepared as aggregates having various macroscopic morphologies (as determined by scanning electron microscopy) in which they are randomly entangled with each other to form entangled balls of fibrils resembling bird nests ("BN"); or as aggregates consisting of bundles of straight to slightly bent or kinked carbon fibrils having substantially the same relative orientation, and having the appearance of combed yarn ("CY") e.g., the longitudinal axis of each fibril (despite individual bends or kinks) extends in the same direction as that of the surrounding fibrils in the bundles; or, as, aggregates consisting of straight to slightly bent or kinked fibrils which are loosely entangled with each other to form an "open net" ("ON") structure. In open net structures the degree of fibril entanglement is greater than observed in the combed yarn aggregates (in which the individual fibrils have substantially the same relative orientation) but less than that of bird nests. CY and ON aggregates are more readily dispersed than BN making them useful in composite fabrication where uniform properties throughout the structure are desired.

When the projection of the graphitic layers on the fibril axis extends for a distance of less than two fibril diameters, the carbon planes of the graphitic nanofiber, in cross section, take on a herring bone appearance. These are termed fishbone fibrils. Geus, U.S. Patent No. 4,855,091, hereby incorporated by reference, provides a procedure for preparation of fishbone fibrils substantially free of a pyrolytic overcoat. These fibrils are also useful in the practice of the invention.

Carbon nanotubes of a morphology similar to the catalytically grown fibrils described above have been grown in a high temperature carbon arc (Iijima, *Nature* 354 56 1991). It is now generally accepted (Weaver,

Science 265 1994) that these arc-grown nanofibers have the same morphology as the earlier catalytically grown fibrils of Tennent. Arc grown carbon nanofibers are also useful in the invention.

5 McCarthy et al., U.S. Patent Application Serial No. 351,967 filed May 15, 1989, hereby incorporated by reference, describes processes for oxidizing the surface of carbon fibrils that include contacting the fibrils with an oxidizing agent that includes sulfuric acid
10 (H_2SO_4) and potassium chlorate ($KClO_3$) under reaction conditions (e.g., time, temperature, and pressure) sufficient to oxidize the surface of the fibril. The fibrils oxidized according to the processes of McCarthy, et al. are non-uniformly oxidized, that is, the carbon
15 atoms are substituted with a mixture of carboxyl, aldehyde, ketone, phenolic and other carbonyl groups.

Fibrils have also been oxidized non-uniformly by treatment with nitric acid. International Application PCT/US94/10168 discloses the formation of oxidized
20 fibrils containing a mixture of functional groups.

Hoogenvaad, M.S., et al. ("Metal Catalysts supported on a Novel Carbon Support", Presented at Sixth International Conference on Scientific Basis for the Preparation of Heterogeneous Catalysts, Brussels, Belgium, September
25 1994) also found it beneficial in the preparation of fibril-supported precious metals to first oxidize the fibril surface with nitric acid. Such pretreatment with acid is a standard step in the preparation of carbon-supported noble metal catalysts, where, given the usual
30 sources of such carbon, it serves as much to clean the surface of undesirable materials as to functionalize it.

In published work, McCarthy and Bening (Polymer Preprints ACS Div. of Polymer Chem. 30 (1) 420(1990)) prepared derivatives of oxidized fibrils in order to
35 demonstrate that the surface comprised a variety of oxidized groups. The compounds they prepared, phenylhydrazones, haloaromaticesters, thallous salts,

etc., were selected because of their analytical utility, being, for example, brightly colored, or exhibiting some other strong and easily identified and differentiated signal. These compounds were not isolated and are, 5 unlike the derivatives described herein, of no practical significance.

While many uses have been found for carbon fibrils and aggregates of carbon fibrils, as described in the patents and patent applications referred to above, 10 many different and important uses may be developed if the fibril surfaces are functionalized. Functionalization, either uniformly or non-uniformly, permits interaction of the functionalized fibrils with various substrates to form unique compositions of matter with unique properties 15 and permits fibril structures to be created based on linkages between the functional sites on the fibrils' surfaces.

OBJECTS OF THE INVENTION

It is therefore a primary object of this 20 invention to provide functionalized fibrils, i.e. fibrils whose surfaces are uniformly or non-uniformly modified so as to have a functional chemical moiety associated therewith.

It is a further and related object of this 25 invention to provide fibrils whose surfaces are functionalized by reaction with oxidizing or other chemical media.

It is a further and related object of this 30 invention to provide fibrils whose surfaces are uniformly modified either by chemical reaction or by physical absorption of species which themselves have a chemical reactivity.

It is a further object to provide fibrils whose 35 surfaces have been modified e.g. by oxidation which are then further modified by reaction with functional groups.

It is still a further and related object of this invention to provide fibrils whose surfaces are

modified with a spectrum of functional groups so that the fibrils can be chemically reacted or physically bonded to chemical groups in a variety of substrates.

It is still the further and related object of 5 this invention to provide complex structures of fibrils by linking functional groups on the fibrils with one another by a range of linker chemistries.

It is still a further and related object of 10 this invention to provide methods for chemical modification of fibril surfaces and methods for physically absorbing species on the surfaces of fibrils so as to provide, in each case, a functional moiety associated with the surface of the fibril.

It is yet a further object of this invention to 15 provide new compositions of matter based upon the functionalized fibrils.

DETAILED DESCRIPTION OF THE INVENTION

These and other objects of the invention are achieved in compositions which broadly have the formula

20 $[C_nH_L]^+R_m^-$

where n is an integer, L is a number less than 0.1n, m is a number less than 0.5n,

each of R is the same and is selected from 25 SO_3H , $COOH$, NH_2 , OH , CHO , CN , $COCl$, halide, $COSH$, SH , $COOR'$, SR' , SiR'_3 , $Si\{OR'\}_yR'^{3-y}$, $Si\{O-SiR'_2\}OR'$, R'' , Li , AlR'_2 , $Hg-X$, TlZ_2 and $Mg-X$,

y is an integer equal to or less than 3,

R' is alkyl, aryl, cycloalkyl or aralkyl,

R'' is fluoroalkyl, fluoroaryl,

30 fluorocycloalkyl, fluoroaralkyl or cycloaryl,

X is halide, and

Z is carboxylate or trifluoroacetate.

The carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic nanotube of 35 substantially constant diameter. The nanotubes include those having a length to diameter ratio of greater than 5 and a diameter of less than 0.5μ , preferably less than

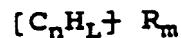
0.1 μ . The nanotubes can also be substantially cylindrical, graphitic nanotubes which are substantially free of pyrolytically deposited carbon, more preferably those characterized by having a projection of the 5 graphite layers on the fibril axis which extends for a distance of at least two fibril diameters and/or those having cylindrical graphitic sheets whose c-axes are substantially perpendicular to their cylindrical axis. These compositions are uniform in that each of R is the 10 same.

Non-uniformly substituted nanotubes are also prepared. These include compositions of the formula



where n, L, m, R and the nanotube itself are as defined 15 above, provided that each of R does not contain oxygen, or, if each of R is an oxygen-containing group COOH is not present.

Functionalized nanotubes having the formula



20 where n, L, m, R and R' have the same meaning as above and the carbon atoms are surface carbon atoms of a fishbone fibril having a length to diameter ratio greater than 5, are also included within the invention. These may be uniformly or non-uniformly substituted. 25 Preferably, the nanotubes are free of thermal overcoat and have diameters less than 0.5 μ .

Also included in the invention are functionalized nanotubes having the formula



30 where n, L, m, R' and R have the same meaning as above. The carbon atoms, C_n, are surface carbons of a substantially cylindrical, graphitic nanotube of substantially constant diameter. The nanotubes have a length to diameter ratio of greater than 5 and a diameter of less than 0.5 μ , preferably less than 0.1 μ . The 35 nanotubes may be nanotubes which are substantially free of pyrolytically deposited carbon. More preferably, the

nanotubes are those in which the projection of the graphite layers on the fibril axes extends for a distance of at least two fibril diameters and/or those having cylindrical graphitic sheets whose c-axes are

5 substantially perpendicular to their cylindrical axis.

In both uniformly and non-uniformly substituted nanotubes, the surface atoms C_n are reacted. Most carbon atoms in the surface layer of a graphitic fibril, as in graphite, are basal plane carbons. Basal plane carbons

10 are relatively inert to chemical attack. At defect sites, where, for example, the graphitic plane fails to extend fully around the fibril, there are carbon atoms analogous to the edge carbon atoms of a graphite plane (See Urry, *Elementary Equilibrium Chemistry of Carbon*,

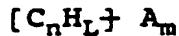
15 Wiley, New York 1989.) for a discussion of edge and basal plane carbons).

At defect sites, edge or basal plane carbons of lower, interior layers of the nanotube may be exposed. The term surface carbon includes all the carbons, basal

20 plane and edge, of the outermost layer of the nanotube, as well as carbons, both basal plane and/or edge, of lower layers that may be exposed at defect sites of the outermost layer. The edge carbons are reactive and must contain some heteroatom or group to satisfy carbon

25 valency.

The substituted nanotubes described above may advantageously be further functionalized. Such compositions include compositions of the formula



30 where the carbons are surface carbons of a nanotube, n, L and m are as described above,

A is selected from

35
$$\begin{array}{cccc} O & O & O & O \\ || & || & || & || \\ OY & NHY & C-OY & C-NR'Y \\ C=O & C=O & C=O & C=O \\ C=Y & C=Y & C=Y & C=Y \end{array}$$
, $-CR'_2-OY$, $N=Y$ or

Y is an appropriate functional group of a protein, a peptide, an enzyme, an antibody, a nucleotide,

an oligonucleotide, an antigen, or an enzyme substrate, enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from R'-OH, R'-NH₂, R'SH, R'CHO, R'CN, R'X, R'SiR'₃, R'Si(OR')_yR'_{3-y}, R'Si(O-SiR'₂)OR', R'-R'', R'-N-CO, (C₂H₄O)_wH, (C₃H₆O)_wH, (C₂H₄O)_w-R', (C₃H₆O)_w-R' and R', and

w is an integer greater than one and less than

200.

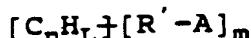
The carbon atoms, C_n, are surface carbons of a substantially cylindrical, graphitic nanotube of substantially constant diameter. The nanotubes include those having a length to diameter ratio of greater than 5 and a diameter of less than 0.1μ, preferably less than 0.05μ. The nanotubes can also be substantially cylindrical, graphitic nanotubes which are substantially free of pyrolytically deposited carbon. More preferably they are characterized by having a projection of the graphite layers on the fibril axes which extends for a distance of at least two fibril diameters and/or they are comprised of cylindrical graphitic sheets whose c-axes are substantially perpendicular to their cylindrical axes. Preferably, the nanotubes are free of thermal overcoat and have diameters less than 0.5μ.

The functional nanotubes of structure

25



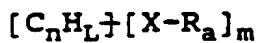
may also be functionalized to produce compositions having the formula



where n, L, m, R' and A are as defined above. The carbon atoms, C_n, are surface carbons of a substantially cylindrical, graphitic nanotube of substantially constant diameter. The nanotubes include those having a length to diameter ratio of greater than 5 and a diameter of less than 0.5μ, preferably less than 0.1μ. The nanotubes can also be substantially cylindrical, graphitic nanotubes which are substantially free of pyrolytically deposited carbon. More preferably they are characterized by having

a projection of the graphite layers on the fibril axes which extends for a distance of at least two fibril diameters and/or by having cylindrical graphitic sheets whose c-axes are substantially perpendicular to their 5 cylindrical axis. Preferably, the nanotubes are free of thermal overcoat and have diameters less than 0.5μ .

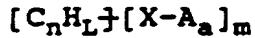
The compositions of the invention also include nanotubes upon which certain cyclic compounds are adsorbed. These include compositions of matter of the 10 formula



where n is an integer, L is a number less than 0.1n, m is less than 0.5n, a is zero or a number less than 10, X is a polynuclear aromatic, polyheteronuclear aromatic or 15 metallocopolyheteronuclear aromatic moiety and R is as recited above. The carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic nanotube of substantially constant diameter. The nanotubes include those having a length to diameter ratio of greater than 5 20 and a diameter of less than 0.5μ , preferably less than 0.1μ . The nanotubes can also be substantially cylindrical, graphitic nanotubes which are substantially free of pyrolytically deposited carbon and more preferably those characterized by having a projection of 25 the graphite layers on said fibril axes which extend for a distance of at least two fibril diameters and/or those having cylindrical graphitic sheets whose c-axes are substantially perpendicular to their cylindrical axes. Preferably, the nanotubes are free of thermal overcoat 30 and have diameters less than 0.5μ .

Preferred cyclic compounds are planar macrocycles as described on p. 76 of Cotton and Wilkinson, *Advanced Organic Chemistry*. More preferred cyclic compounds for adsorption are porphyrins and 35 phthalocyanines.

The adsorbed cyclic compounds may be functionalized. Such compositions include compounds of the formula



5 where m, n, L, a, X and A are as defined above and the carbons are surface carbons of a substantially cylindrical graphitic nanotube as described above.

The carbon fibrils functionalized as described above may be incorporated in a matrix. Preferably, the 10 matrix is an organic polymer (e.g., a thermoset resin such as epoxy, bismaleimide, polyamide, or polyester resin; a thermoplastic resin; a reaction injection molded resin; or an elastomer such as natural rubber, styrene-butadiene rubber, or cis-1,4-polybutadiene); an inorganic 15 polymer (e.g., a polymeric inorganic oxide such as glass), a metal (e.g., lead or copper), or a ceramic material (e.g., Portland cement).

Without being bound to a particular theory, the functionalized fibrils are better dispersed into polymer 20 systems because the modified surface properties are more compatible with the polymer, or, because the modified functional groups (particularly hydroxyl or amine groups) are bonded directly to the polymer as terminal groups. In this way, polymer systems such as polycarbonates, 25 polyurethanes, polyesters or polyamides/imides bond directly to the fibrils making the fibrils easier to disperse with improved adherence.

The invention is also in methods of introducing functional groups onto the surface of carbon fibrils by 30 contacting carbon fibrils with a strong oxidizing agent for a period of time sufficient to oxidize the surface of said fibrils and further contacting said fibrils with a reactant suitable for adding a functional group to the oxidized surface. In a preferred embodiment of the 35 invention, the oxidizing agent is comprised of a solution of an alkali metal chlorate in a strong acid. In other embodiments of the invention the alkali metal chlorate is

sodium chlorate or potassium chlorate. In preferred embodiments the strong acid used is sulfuric acid. Periods of time sufficient for oxidation are from about 0.5 hours to about 24 hours.

5 The invention is also in methods for producing a network of carbon fibrils comprising contacting carbon fibrils with an oxidizing agent for a period of time sufficient to oxidize the surface of the carbon fibrils, contacting the surface-oxidized carbon fibrils with
10 reactant suitable for adding a functional group to the surface of the carbon fibrils, and further contacting the surface-functionalized fibrils with a cross-linking agent effective for producing a network of carbon fibrils. A preferred cross-linking agent is a polyol, polyamine or
15 polycarboxylic acid.

Functionalized fibrils also are useful for preparing rigid networks of fibrils. A well-dispersed, three-dimensional network of acid-functionalized fibrils may, for example, be stabilized by cross-linking the acid
20 groups (inter-fibril) with polyols or polyamines to form a rigid network.

The invention also includes three-dimensional networks formed by linking functionalized fibrils of the invention. These complexes include at least two
25 functionalized fibrils linked by one or more linkers comprising a direct bond or chemical moiety. These networks comprise porous media of remarkably uniform equivalent pore size. They are useful as adsorbents, catalyst supports and separation media.

30 Although the interstices between these fibrils are irregular in both size and shape, they can be thought of as pores and characterized by the methods used to characterize porous media. The size of the interstices in such networks can be controlled by the concentration
35 and level of dispersion of fibrils, and the concentration and chain lengths of the cross-linking agents. Such materials can act as structured catalyst supports and may

be tailored to exclude or include molecules of a certain size. Aside from conventional industrial catalysis, they have special applications as large pore supports for biocatalysts.

5 The rigid networks can also serve as the backbone in biomimetic systems for molecular recognition. Such systems have been described in US Patent No. 5,110,833 and International Patent Publication No. WO93/19844. The appropriate choices for cross-linkers 10 and complexing agents allow for stabilization of specific molecular frameworks.

METHODS OF FUNCTIONALIZING FIBRILS

The uniformly functionalized fibrils of the invention can be directly prepared by sulfonation, 15 electrophilic addition to deoxygenated fibril surfaces or metallation. When arc grown nanofibers are used, they may require extensive purification prior to functionalization. Ebbesen et al. (Nature 367 519 (1994)) give a procedure for such purification.

20 Preferably, the carbon fibrils are processed prior to contacting them with the functionalizing agent. Such processing may include dispersing the fibrils in a solvent. In some instances the carbon fibrils may then be filtered and dried prior to further contact.

1. SULFONATION

Background techniques are described in March, J.P., *Advanced Organic Chemistry*, 3rd Ed. Wiley, New York 1985; House, H., *Modern Synthetic Reactions*, 2nd Ed., Benjamin/Cummings, Menlo Park, CA 1972.

30 Activated C-H (including aromatic C-H) bonds can be sulfonated using fuming sulfuric acid (oleum), which is a solution of conc. sulfuric acid containing up to 20% SO₃. The conventional method is via liquid phase at T-80°C using oleum; however, activated C-H bonds can 35 also be sulfonated using SO₃ in inert, aprotic solvents, or SO₃ in the vapor phase. The reaction is:



Over-reaction results in formation of sulfones, according to the reaction:



EXAMPLE 1

5 Activation of C-H Bonds Using Sulfuric Acid

Reactions were carried out in the gas phase and in solution without any significant difference in results. The vapor phase reaction was carried out in a horizontal quartz tube reactor heated by a Lindberg 10 furnace. A multi-neck flask containing 20% SO_3 in conc. H_2SO_4 fitted with gas inlet/outlet tubes was used as the SO_3 source.

A weighed sample of fibrils (BN or CC) in a porcelain boat was placed in the 1" tube fitted with a 15 gas inlet; the outlet was connected to a conc. H_2SO_4 bubbler trap. Argon was flushed through the reactor for 20 min to remove all air, and the sample was heated to 300°C for 1 hour to remove residual moisture. After drying, the temperature was adjusted to reaction 20 temperature under argon.

When the desired temperature was stabilized, the SO_3 source was connected to the reactor tube and an argon stream was used to carry SO_3 vapors into the quartz tube reactor. Reaction was carried out for the desired 25 time at the desired temperature, after which the reactor was cooled under flowing argon. The fibrils were then dried at 90°C at 5" Hg vacuum to obtain the dry weight gain. Sulfonic acid ($-SO_3H$) content was determined by reaction with 0.100N NaOH and back-titration with 0.100N 30 HCl using pH 6.0 as the end point.

The liquid phase reaction was carried out in conc. sulfuric acid containing 20% SO_3 in a multi-neck 100 cc flask fitted with a thermometer/temperature controller and a magnetic stirrer. A fibril slurry in 35 conc. H_2SO_4 (50) was placed in the flask. The oleum solution (20 cc) was preheated to ~60°C before addition to the reactor. After reaction, the acid slurry was

10 poured onto cracked ice, and diluted immediately with 1 l DI water. The solids were filtered and washed exhaustively with DI water until there was no change in pH of the wash effluent. Fibrils were dried at 100°C at 5 5" Hg vacuum. Due to transfer losses on filtration, accurate weight gains could not be obtained. Results are listed in Table 1.

TABLE I

10

Summary of Reactions

EX.	RUN #	REACT	SAMPLE Wt.g	FIBRIL TYPE	T°C	TIME	DRY Wt GAIN	SO ₃ H CONC meq/g
	1A	118-60A	Vap	0.20	CY	110	15 m	9.3% 0.50
	1B	118-61A	Vap	0.20	BN	100	30 m	8.5% 0.31
15	1C	118-61B	Vap	0.20	BN	65	15 m	4.2% 0.45
	1D	118-56A	Liq	1.2	CY	50	10 m	0.33
	1E	118-56B	Liq	1.0	CY	25	20 m	0.40

20 There was no significant difference in sulfonic acid content by reaction in the vapor phase or liquid phase. There was a temperature effect. Higher temperature of reaction (vapor phase) gives higher amounts of sulfones. In 118-61B, the 4.2% wt gain agreed with the sulfonic acid content (theoretical was 0.51 meq/g). Runs 60A and 61A had too high a wt gain to be accounted for solely by sulfonic acid content. It was therefore assumed that appreciable amounts of sulfones were also made.

2. ADDITIONS TO OXIDE-FREE FIBRIL SURFACES

30 Background techniques are described in Urry, G., *Elementary Equilibrium Chemistry of Carbon*, Wiley, New York 1989.

35 The surface carbons in fibrils behave like graphite, i.e., they are arranged in hexagonal sheets containing both basal plane and edge carbons. While basal plane carbons are relatively inert to chemical attack, edge carbons are reactive and must contain some heteroatom or group to satisfy carbon valency. Fibrils

also have surface defect sites which are basically edge carbons and contain heteroatoms or groups.

The most common heteroatoms attached to surface carbons of fibrils are hydrogen, the predominant gaseous component during manufacture; oxygen, due to its high reactivity and because traces of it are very difficult to avoid; and H₂O, which is always present due to the catalyst. Pyrolysis at ~1000°C in a vacuum will deoxygenate the surface in a complex reaction with unknown mechanism, but with known stoichiometry. The products are CO and CO₂, in a 2:1 ratio. The resulting fibril surface contains radicals in a C₁-C₄ alignment which are very reactive to activated olefins. The surface is stable in a vacuum or in the presence of an inert gas, but retains its high reactivity until exposed to a reactive gas. Thus, fibrils can be pyrolyzed at ~1000°C in vacuum or inert atmosphere, cooled under these same conditions and reacted with an appropriate molecule at lower temperature to give a stable functional group.

20 Typical examples are:

1000°C

Fibril-O -----> Reactive Fibril Surface (RFS) + 2 CO + CO₂

followed by:

25 RFS + CH₂=CHCOX -----> Fibril-R'COX X==OH, -Cl, -NH₂, -H

RFS + Maleic anhydride -----> Fibril-R'(COOH)₂

RFS + Cyanogen -----> Fibril-CN

30 RFS + CH₂=CH-CH₂X -----> Fibril-R'CH₂X X==NH₂, -OH, -Halogen,

RFS + H₂O -----> Fibril=O (quinoidal)

RFS + CH₂=CHCHO -----> Fibril-R'CHO (aldehydic)

RFS + CH₂=CH-CN -----> Fibril-R'CN

35

where R' is a hydrocarbon radical (alkyl, cycloalkyl, etc.)

EXAMPLE 2

**Preparation of Functionalized Fibrils by Reacting
Acrylic Acid with Oxide-Free Fibril Surfaces**

One gram of BN fibrils in a porcelain boat is placed in a horizontal 1" quartz tube fitted with a 5 thermocouple and situated in a Lindberg tube furnace. The ends are fitted with a gas inlet/outlets. The tube is purged with dry, deoxygenated argon for 10 minutes, after which the temperature of the furnace is raised to 300°C and held for 30 minutes. Thereafter, under a 10 continued flow of argon, the temperature is raised in 100°C increments to 1000°C, and held there for 16 hours. At the end of that time, the tube is cooled to room temperature (RT) under flowing argon. The flow of argon is then shunted to pass through a multi-neck flask 15 containing neat purified acrylic acid at 50°C and fitted with gas inlet/outlets. The flow of acrylic acid/argon vapors is continued at RT for 6 hours. At the end of that time, residual unreacted acrylic acid is removed, first by purging with argon, then by vacuum drying at 20 100°C at <5" vacuum. The carboxylic acid content is determined by reaction with excess 0.100N NaOH and back-titrating with 0.100N HCl to an endpoint at pH 7.5.

EXAMPLE 3

**Preparation of Functionalized Fibrils by Reacting
Acrylic Acid with Oxide-Free Fibril Surfaces**

The procedure is repeated in a similar manner to the above procedure, except that the pyrolysis and cool-down are carried out at 10^{-4} Torr vacuum. Purified acrylic acid vapors are diluted with argon as in the 30 previous procedure.

EXAMPLE 4

**Preparation of Functionalized Fibrils by Reacting
Maleic Acid with Oxide-Free Fibril Surfaces**

The procedure is repeated as in Ex.2, except 35 that the reactant at RT is purified maleic anhydride (MAN) which is fed to the reactor by passing argon gas through a molten MAN bath at 80°C.

EXAMPLE 5

Preparation of Functionalized Fibrils by Reacting Acryloyl Chloride with Oxido-Free Fibril Surfaces

The procedure is repeated as in Ex. 2, except 5 that the reactant at RT is purified acryloyl chloride, which is fed to the reactor by passing argon over neat acryloyl chloride at 25°C. Acid chloride content is determined by reaction with excess 0.100N NaOH and back-titration with 0.100N HCl.

10 Pyrolysis of fibrils in vacuum deoxygenates the fibril surface. In a TGA apparatus, pyrolysis at 1000°C either in vacuum or in a purified Ar flow gives an average wt loss of 3% for 3 samples of BN fibrils. Gas chromatographic analyses detected only CO and CO₂, in 15 -2:1 ratio, respectively. The resulting surface is very reactive and activated olefins such as acrylic acid, acryloyl chloride, acrylamide, acrolein, maleic anhydride, allyl amine, allyl alcohol or allyl halides will react even at room temperature to form clean 20 products containing only that functionality bonded to the activated olefin. Thus, surfaces containing only carboxylic acids are available by reaction with acrylic acid or maleic anhydride; surf only acid chloride by reaction with acryloyl chloride; only aldehyde from 25 acrolein; only hydroxyl from allyl alcohol; only amine from allyl amine, and only halide from allyl halide.

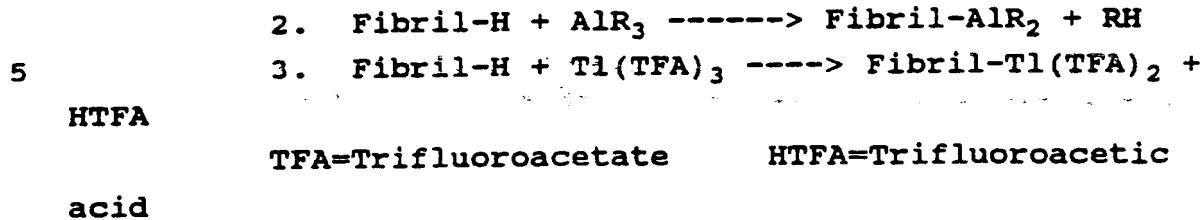
3. METALLATION

Background techniques are given in March, Advanced Organic Chemistry, 3rd ed., p 545

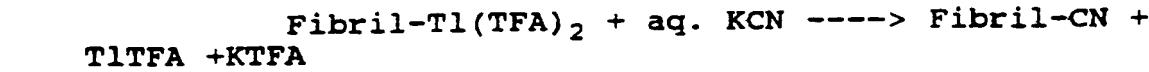
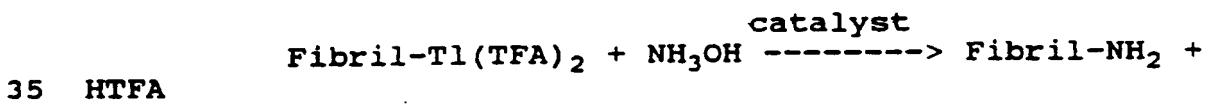
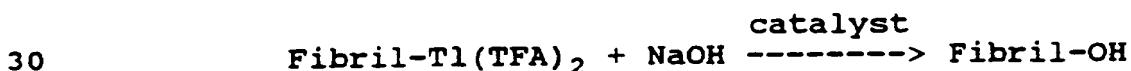
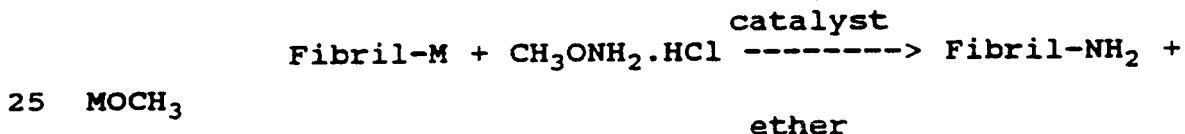
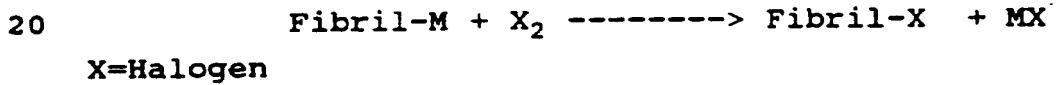
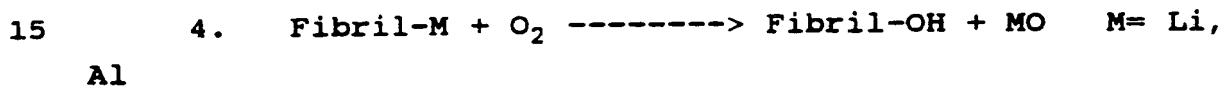
30 Aromatic C-H bonds can be metallated with a variety of organometallic reagents to produce carbon-metal bonds (C-M). M is usually Li, Be, Mg, Al, or Tl; however, other metals can also be used. The simplest reaction is by direct displacement of hydrogen in 35 activated aromatics:



The reaction may require additionally, a strong base, such as potassium *t*-butoxide or chelating diamines. Aprotic solvents are necessary (paraffins, benzene).



The metallated derivatives are examples of primary singly-functionalized fibrils. However, they can be reacted further to give other primary singly-functionalized fibrils. Some reactions can be carried out sequentially in the same apparatus without isolation of intermediates.



EXAMPLE 6

Preparation of Fibril-Li

One gram of CC fibrils is placed in a porcelain boat and inserted into a 1" quartz tube reactor which is enclosed in a Lindberg tube furnace. The ends of the tube are fitted with gas inlet/outlets. Under continuous flow of H₂, the fibrils are heated to 700°C for 2 hours to convert any surface oxygenates to C-H bonds. The reactor is then cooled to RT under flowing H₂.

The hydrogenated fibrils are transferred with dry, de-oxygenated heptane (with LiAlH₄) to a 1 liter multi-neck round bottom flask equipped with a purified argon purging system to remove all air and maintain an inert atmosphere, a condenser, a magnetic stirrer and rubber septum through which liquids can be added by a syringe. Under an argon atmosphere, a 2% solution containing 5 mmol butyllithium in heptane is added by syringe and the slurry stirred under gentle reflux for 4 hours. At the end of that time, the fibrils are separated by gravity filtration in an argon atmosphere glove box and washed several times on the filter with dry, deoxygenated heptane. Fibrils are transferred to a 50 cc r.b. flask fitted with a stopcock and dried under 10⁻⁴ torr vacuum at 50°C. The lithium concentration is determined by reaction of a sample of fibrils with excess 0.100N HCl in DI water and back-titration with 0.100N NaOH to an endpoint at pH 5.0.

EXAMPLE 7Preparation of Fibril-Tl(TFA)₂

One gram of CC fibrils are hydrogenated as in Ex. 5 and loaded into the multi-neck flask with HTFA which has been degassed by repeated purging with dry argon. A 5% solution of 5 mmol Tl(TFA)₃ in HTFA is added to the flask through the rubber septum and the slurry is stirred at gentle reflux for 6 hours. After reaction, the fibrils are collected and dried as in Ex. 1.

EXAMPLE 8

**Preparation of Fibril-OH
(Oxygenated derivative containing only OH
functionalization)**

One half g of lithiated fibrils prepared in

5 Ex. 6 are transferred with dry, deoxygenated heptane in an argon-atmosphere glove bag to a 50 cc single neck flask fitted with a stopcock and magnetic stirring bar. The flask is removed from the glove bag and stirred on a magnetic stirrer. The stopcock is then opened to the air

10 and the slurry stirred for 24 hours. At the end of that time, the fibrils are separated by filtration and washed with aqueous MeOH, and dried at 50°C at 5" vacuum. The concentration of OH groups is determined by reaction with a standardized solution of acetic anhydride in dioxane

15 (0.252 M) at 80°C to convert the OH groups to acetate esters, in so doing, releasing 1 equivalent of acetic acid/mole of anhydride reacted. The total acid content, free acetic acid and unreacted acetic anhydride, is determined by titration with 0.100N NaOH to an endpoint

20 at pH 7.5.

EXAMPLE 9

Preparation of Fibril-NH₂

One gram of thallated fibrils is prepared as in Ex. 7. The fibrils are slurried in dioxane and 0.5 g

25 triphenyl phosphine dissolved in dioxane is added. The slurry is stirred at 50°C for several minutes, followed by addition at 50°C of gaseous ammonia for 30 min. The fibrils are then separated by filtration, washed in dioxane, then DI water and dried at 80°C at 5" vacuum.

30 The amine concentration is determined by reaction with excess acetic anhydride and back-titration of free acetic acid and unreacted anhydride with 0.100N NaOH.

**4. DERIVATIZED POLYNUCLEAR AROMATIC, POLYHETERONUCLEAR
AROMATIC AND PLANAR MACROCYCLIC COMPOUNDS**

35 The graphitic surfaces of fibrils allow for physical adsorption of aromatic compounds. The attraction is through van der Waals forces. These forces

are considerable between multi-ring heteronuclear aromatic compounds and the basal plane carbons of graphitic surfaces. Desorption may occur under conditions where competitive surface adsorption is possible or where the adsorbate has high solubility.

EXAMPLE 10

Adsorption of Porphyrins and phthalocyanines onto Fibrils

The preferred compounds for physical adsorption on fibrils are derivatized porphyrins or phthalocyanines which are known to adsorb strongly on graphite or carbon blacks. Several compounds are available, e.g., a tetracarboxylic acid porphyrin, cobalt (II) phthalocyanine or dilithium phthalocyanine. The latter two can be derivatized to a carboxylic acid form.

The loading capacity of the porphyrin or phthalocyanines can be determined by decoloration of solutions when they are added incrementally. The deep colors of the solutions (deep pink for the tetracarboxylic acid porphyrin in MeOH, dark blue-green for the Co(II) or the dilithium phthalocyanine in acetone or pyridine) are discharged as the molecules are removed by adsorption onto the black surface of the fibrils.

Loading capacities were estimated by this method and the footprints of the derivatives were calculated from their approximate measurements (~140 sq. Angstroms). For an average surface area for fibrils of $250 \text{ m}^2/\text{g}$, maximum loading will be ~0.3 mmol/g.

The tetracarboxylic acid porphyrin was analyzed by titration. The integrity of the adsorption was tested by color release in aqueous systems at ambient and elevated temperatures.

The fibril slurries were initially mixed (Waring blender) and stirred during loading. Some of the slurries were ultra-sounded after color was no longer discharged, but with no effect.

After loading, Runs 169-11, -12, -14 and -19-1 (see Table II) were washed in the same solvent to remove

occluded pigment. All gave a continuous faint tint in the wash effluent, so it was difficult to determine the saturation point precisely. Runs 168-18 and -19-2 used the calculated amounts of pigment for loading and were 5 washed only very lightly after loading.

The tetracarboxylic acid porphyrin (from acetone) and the Co phthalocyanine (from pyridine) were loaded onto fibrils for further characterization (Runs 169-18 and -19-2, respectively).

10 Analysis of Tetracarboxylic Acid Porphyrin

Addition of excess base (pH 11-12) caused an immediate pink coloration in the titrating slurry. While this did not interfere with the titration, it showed that at high pH, porphyrin desorbed. The carboxylic acid 15 concentration was determined by back titration of excess NaOH using Ph 7.5 as end-point. The titration gave a loading of 1.10 meq/g of acid, equivalent to 0.275 meq/g porphyrin.

Analysis of Cobalt or Dilithium Phthalocyanine

20 The concentrations of these adsorbates were estimated from decoloration experiments only. The point where the blue-green tint did not fade after 30 min was taken as the saturation-point.

A number of substituted polynuclear aromatic or 25 polyheteronuclear aromatic compounds were adsorbed on fibril surfaces. For adhesion, the number of aromatic rings should be greater than two per rings/pendant functional group. Thus, substituted anthracenes, phenanthrenes, etc., containing three fused rings, or 30 polyfunctional derivatives containing four or more fused rings can be used in place of the porphyrin or phthalocyanine derivatives. Likewise, substituted aromatic heterocycles such as the quinolines, or multiply substituted heteroaromatics containing four or more rings 35 can be used.

Table II summarizes the results of the loading experiments for the three porphyrin/phthalocyanine derivatives.

5

TABLE II
Summary of Adsorption Runs

EX.	RUN #	Adsorbate	Wgt.		Loading		meq/g
			Fib. g	Solv. g/g	Form	Titration	
10A	169-11	TCAPorph	19.6 mg	Acet	0.18g/g	Acid	na
10B	169-12	TCAPorph	33.3 mg	H ₂ O	0.11	Na Salt	na
10C	169-14	DiliPhth	119.0 mg	Acet	0.170	Li	na
10D	169-19-1	CoPhth	250.0 mg	Pyr	0.187	Co	0.335(cal)
10E	169-18	TCAPorph	1.00 g	Acet	0.205	Acid	1.10(T)
10F	169-19-2	CoPhth	1.40 g	Pyr	0.172	Co	0.303(cal)

5. CHLORATE OR NITRIC ACID OXIDATION

Literature on the oxidation of graphite by

20 strong oxidants such as potassium chlorate in conc. sulfuric acid or nitric acid, includes R.N. Smith, Quarterly Review 13, 287 (1959); M.J.D. Low, Chem. Rev. 60, 267 (1960)). Generally, edge carbons (including defect sites) are attacked to give mixtures of carboxylic acids, phenols and other oxygenated groups. The mechanism is complex involving radical reactions.

EXAMPLE 11

Preparation of Carboxylic Acid-Functionalized Fibrils Using Chlorate.

30 Fibrils Using Chlorate.

The sample of CC fibrils was slurried in conc. H_2SO_4 by mixing with a spatula and then transferred to a reactor flask fitted with gas inlet/outlets and an overhead stirrer. With stirring and under a slow flow of argon, the charge of $NaClO_3$ was added in portions at RT over the duration of the run. Chlorine vapors were generated during the entire course of the run and were

swept out of the reactor into a aqueous NaOH trap. At the end of the run, the fibril slurry was poured over cracked ice and vacuum filtered. The filter cake was then transferred to a Soxhlet thimble and washed in a 5 Soxhlet extractor with DI water, exchanging fresh water every several hours. Washing was continued until a sample of fibrils, when added to fresh DI water, did not change the pH of the water. The fibrils were then separated by filtration and dried at 100°C at 5" vacuum 10 overnight.

The carboxylic acid content was determined by reacting a sample with excess 0.100N NaOH and back-titrating with 0.100ⁿ HCl to an endpoint at pH 7.5. The results are listed in the Table.

15

TABLE IIISummary of Direct Oxidation Runs

20	Rec Acid, Ex. RUN #	<u>Components, g</u>			<u>Time</u>		
		Fibrils meq/g	NaClO ₃ cc	H ₂ SO ₄	hours	Wash Ph	Wgt
25	11A 168-30	10.0	8.68	450	24	5.7	
	10.0 0.78						
	11B 168-36	12.0	13.9	600	24	5.9	
	13.7 0.75						

30

EXAMPLE 12Preparation of Carboxylic Acid-Functionalized
Fibrils Using Nitric Acid.

A weighed sample of fibrils was slurried with 35 nitric acid of the appropriate strength in a bound bottom multi-neck indented reactor flask equipped with an overhead stirrer and a water condenser. With constant stirring, the temperature was adjusted and the reaction carried out for the specified time. Brown fumes were 40 liberated shortly after the temperature exceeded 70°C, regardless of acid strength. After the reaction, the slurry was poured onto cracked ice and diluted with DI water. The slurry was filtered and excess acid removed

by washing in a Soxhlet extractor, replacing the reservoir with fresh DI water every several hours, until a slurried sample gave no change in Ph from DI water. The fibrils were dried at 100°C at 5" vacuum overnight.

5 A weighed portion of fibrils was reacted with standard 0.100 N NaOH and the carboxylic acid content determined by back-titration with 0.100 N HCl. Surface oxygen content was determined by XPS. Dispersibility in water was tested at 0.1 wt% by mixing in a Waring Blender at

10 high for 2 min. Results are summarized in Table 4.

TABLE IV

Summary of Direct Oxidation Runs

15	COMPONENTS									
	Disp	Gms.	cc	Acid	Temp.	Time	Wgt.	COOH	ESCA, at%	
		Ex.	Fibrils	Acid	Conc.				C	O
20	H ₂ O	12A P	1(BN)	300	70%	RT	24 hr	0	<0.1	98 2
25		12B P	1(BN)	300	15	rflx	48	<5%	<0.1	not analyzed
		12C G	20(BN)	1.0 1	70	rflx	7	25%	0.8	not analyzed
30		12D G	48(BN)	1.0 1	70	rflx	7	20%	0.9	not analyzed

P=Poor; G=Good

35 6. SECONDARY DERIVATIVES OF FUNCTIONALIZED FIBRILS

Carboxylic Acid-functionalized Fibrils

The number of secondary derivatives which can be prepared from just carboxylic acid is essentially limitless. Alcohols or amines are easily linked to acid 40 to give stable esters or amides. If the alcohol or amine is part of a di- or poly-functional molecule, then linkage through the O- or NH- leaves the other functionalities as pendant groups. Typical examples of secondary reagents are:

	<u>GENERAL FORMULA</u>	<u>PENDANT GROUP</u>	<u>EXAMPLES</u>
5	HO-R, R=alkyl, aralkyl, aryl, fluoroethanol, polymer, SiR ₃	R-	Methanol, phenol, trifluorocarbon, OH-terminated Polyester, silanols
	H ₂ N-R R=same as above	R-	Amines, anilines, fluorinated amines, silylamines, amine terminated polyamides
10	Cl-SiR ₃	SiR ₃ -	Chlorosilanes
	HO-R-OH, R=alkyl, aralkyl, CH ₂ O-	HO-	Ethyleneglycol, PEG, Pentaerythritol, bis-Phenol A
15	H ₂ N-R-NH ₂ , R=alkyl, aralkyl	H ₂ N-	Ethylenediamine, polyethylenamines
20	X-R-Y, R=alkyl, etc; X=OH Y- or NH ₂ ; Y=SH, CN, C=O, CHO, alkene, alkyne, aromatic, heterocycles		Polyamine amides, Mercaptoethanol

The reactions can be carried out using any of the methods developed for esterifying or aminating carboxylic acids with alcohols or amines. Of these, the 25 methods of H.A. Staab, *Angew. Chem. Internat. Edit.*, (1), 351 (1962) using N,N'-carbonyl diimidazole (CDI) as the acylating agent for esters or amides, and of G.W. Anderson, et al., *J. Amer. Chem. Soc.* 86, 1839 (1964), using N-Hydroxysuccinimide (NHS) to activate carboxylic acids for amidation were used.

EXAMPLE 13

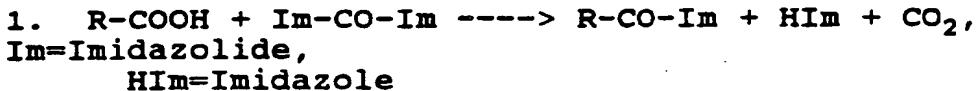
Preparation of Secondary Derivatives of Functionalized Fibrils

N, N'-Carbonyl Diimidazole

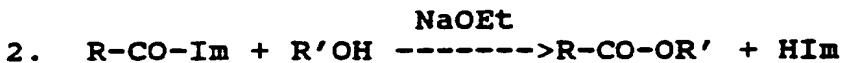
35 Clean, dry, aprotic solvents (e.g., toluene or dioxane) are required for this procedure. Stoichiometric amounts of reagents are sufficient. For esters, the carboxylic acid compound is reacted in an inert atmosphere (argon) in toluene with a stoichiometric

amount of CDI dissolved in toluene at R.T. for 2 hours. During this time, CO_2 is evolved. After two hours, the alcohol is added along with catalytic amounts of Na ethoxide and the reaction continued at 80°C for 4 hr.

5 For normal alcohols, the yields are quantitative. The reactions are:



10



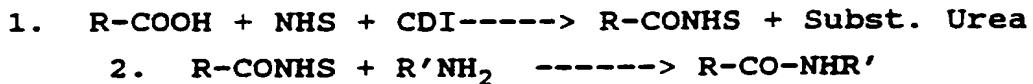
Amidation of amines occurs uncatalyzed at RT.

15 The first step in the procedure is the same. After evolution of CO_2 , a stoichiometric amount of amine is added at RT and reacted for 1-2 hours. The reaction is quantitative. The reaction is:



20 N-Hydroxysuccinimide

Activation of carboxylic acids for amination with primary amines occurs through the N-hydroxysuccinamyl ester; carbodiimide is used to tie up the water released as a substituted urea. The NHS ester is then converted at RT to the amide by reaction with primary amine. The reactions are:



Silylation

30 Trialkylsilylchlorides or trialkylsilanols react immediately with acidic H according to:



Small amounts of Diaza-1,1,1-bicyclooctane (DABCO) are used as catalysts. Suitable solvents are 35 dioxane and toluene.

EXAMPLE 14

**Preparation of Ester/Alcohol Derivatives
from Carboxylic Acid-Functionalized Fibrils**

The carboxylic acid functionalized fibrils were 40 prepared as in Example 11. The carboxylic acid content

was 0.75 meq/g. Fibrils were reacted with a stoichiometric amount of CDI in an inert atmosphere with toluene as solvent at R.T. until CO₂ evolution ceased. Thereafter, the slurry was reacted at 80 °C with a 10-
5 fold molar excess of polyethyleneglycol (MW 600) and a small amount of NaOEt as catalyst. After two hours reaction, the fibrils were separated by filtration, washed with toluene and dried at 100 °C.

EXAMPLE 15

10 Preparation of Amide/Amine Derivatives
from Carboxylic Acid-Functionalized Fibrils (177-041-1)
0.242 g of chlorate-oxidized fibrils (0.62
meq/g) was suspended in 20 ml anhydrous dioxane with
stirring in a 100 ml RB flask fitted with a serum
15 stopper. A 20-fold molar excess of N-Hydroxysuccinimide
(0.299 g) was added and allowed to dissolve. This was
followed by addition of 20-fold molar excess of 1-ethyl-
3-(3-dimethylaminopropyl)-carbodiimide (EDAC) (0.510 g),
and stirring was continued for 2 hr at RT. At the end of
20 this period stirring was stopped, and the supernatant
aspirated and the solids were washed with anhydrous
dioxane and MeOH and filtered on a 0.45 micron
polysulfone membrane. The solids were washed with
additional MeOH on the filter membrane and vacuum-dried
25 until no further weight reduction was observed. Yield of
NHS-activated oxidized fibrils was 100% based on the 6%
weight gain observed.

100 µl ethylenediamine (en) was added to 10 ml
0.2 M NaHCO₃ buffer. An equivalent volume of acetic acid
30 (HOAc) was added to maintain the pH near 8. NHS-
activated oxidized fibrils (0.310 g) was added with
vigorous stirring and reacted for 1 hr. An additional
300 µl of en and 300 µl HOAc was added for an additional
10 min. The solution was filtered on 0.45 micron
35 polysulfone membrane and washed successively with NaHCO₃
buffer, 1% HCl, DI water and EtOH. The solids were dried
under vacuo overnight. The HCl salt was converted back

to the free amine by reaction with NaOH (177-046-1) for further analysis and reactions.

ESCA was carried out to quantify the amount of N present on the aminated fibrils (GF/NH₂). ESCA analysis of 177-046-1 showed 0.90 at% N (177-059). To further assess how much of this N is present as both accessible and reactive amine groups, a derivative was made by the gas phase reaction with pentafluorobenzaldehyde to produce the corresponding Schiff Base linkages with available primary amine groups. ESCA analysis still showed the 0.91 at% N, as expected, and 1.68 at%F. This translates into a 0.34 at% of N present as reactive primary amine on the aminated fibrils (5 F per pentafluorobenzaldehyde molecule). A level of 0.45 at% N would be expected assuming complete reaction with the free ends of each N. The observed level indicates a very high yield from the reaction of N with NHS-activated fibril and confirms the reactivity of the available free amine groups.

At the level of 0.34 at% N present as free amine calculated from the ESCA data, there would be almost complete coverage of the fibrils by the free amine groups allowing coupling of other materials.

EXAMPLE 16

25 **Preparation of Silyl Derivative
from Carboxylic Acid-Functionalized Fibrils**

Acid functionalized fibrils prepared as in Example 11 were slurried in dioxane in an inert atmosphere. With stirring, a stoichiometric amount of 30 chlorotriethyl silane was added and reacted for 0.5 hr, after which several drops of a 5% solution of DABCO in dioxane was added. The system was reacted for an additional hour, after which the fibrils were collected by filtration and washed in dioxane. The fibrils were 35 dried at 100°C in 5" vacuum overnight.

Table 5 summarizes the secondary derivative preparations. The products were analyzed by ESCA for C, O, N, Si and F surface contents.

TABLE V

5

Summary of Secondary Derivative Preparations

	REACTANT	PENDANT GROUP	ESCA ANALYSIS, ATOM %					
			S	C	N	O	Si	F
	As Grown	-----	--	98.5	--	1.5	--	--
10	Chlorate Oxidized	-COOH, C=O, C-OH	--	92.4	--	7.6	--	--
	$\text{H}_2\text{N}-\text{C}_2\text{H}_4-\text{NH}_2$	-CONHC ₂ H ₄ NH ₂	--	99.10	0.90	--	--	--
15		-CONHC ₂ H ₄ N=OC ₆ F ₅	--	97.41	0.91	--	--	1.68

EXAMPLE 17

20

Preparation of Silyl Derivative
from Carboxylic Acid-Functionalized Fibrils

Acid functionalized fibrils prepared as in Example 11 are slurried in dioxane in an inert atmosphere. With stirring, a stoichiometric amount of 25 chlorotriethyl silane is added and reacted for 0.5 hr, after which several drops of a 5% solution of DABCO in dioxane is added. The system is reacted for an additional hour, after which the fibrils are collected by filtration and washed in dioxane. The fibrils are dried 30 at 100°C in 5" vacuum overnight.

Table VI summarizes the secondary derivative preparations. Products are analyzed by ESCA. The analysis confirms the incorporation of the desired pendant groups. The products are analyzed by ESCA for C, 35 O, N, Si and F surface contents.

TABLE VISummary of Secondary Derivative Preparations

5	REACTANT	PENDANT GROUP	S	ESCA ANALYSIS, ATOM %				
				C	N	O	Si	F
	$\text{CF}_3\text{CH}_2\text{OH}$	$-\text{COOCH}_2\text{CF}_3$						NOT ANALYZED
	PolyEG-600	$-\text{CO}-(\text{OC}_2\text{H}_4\text{O}-)\text{H}$						NOT ANALYZED
10	$\text{HO}-\text{C}_2\text{H}_4-\text{SH}$	$-\text{COOC}_2\text{H}_4\text{SH}$						
	$\text{Cl}-\text{SiEt}_3$	$-\text{COSiEt}_3$						

Sulfonic Acid-Functionalized Fibrils

15 Aryl sulfonic acids, as prepared in Example 1 can be further reacted to yield secondary derivatives. Sulfonic acids can be reduced to mercaptans by LiAlH_4 or the combination of triphenyl phosphine and iodine (March, J.P., p. 1107). They can also be converted to sulfonate esters by reaction with dialkyl ethers, i.e., Fibril--
 20 $\text{SO}_3\text{H} + \text{R-O-R} \longrightarrow \text{Fibril-SO}_2\text{OR} + \text{ROH}$

Fibrils Functionalized by Electrophilic Addition to Oxygen-Free Fibril Surfaces or by Metallization

25 The primary products obtainable by addition of activated electrophiles to oxygen-free fibril surfaces have pendant $-\text{COOH}$, $-\text{COCl}$, $-\text{CN}$, $-\text{CH}_2\text{NH}_2$, $-\text{CH}_2\text{CH}$, $-\text{CH}_2-$ Halogen, or HC=O . These can be converted to secondary derivatives by the following:

30 Fibril- COOH \longrightarrow see above.

Fibril- COCl (acid chloride) + $\text{HO-R-Y} \longrightarrow \text{F-COO-R-Y}$
 (Sec. 4/5)

Fibril- $\text{COCl} + \text{NH}_2-\text{R-Y} \longrightarrow \text{F-CONH-R-Y}$

Fibril- $\text{CN} + \text{H}_2 \longrightarrow \text{F-CH}_2-\text{NH}_2$

35 Fibril- $\text{CH}_2\text{NH}_2 + \text{HOOC-R-Y} \longrightarrow \text{F-CH}_2\text{NHCO-R-Y}$

Fibril- $\text{CH}_2\text{NH}_2 + \text{O=CR-R'Y} \longrightarrow \text{F-CH}_2\text{N=CR-R'-Y}$

Fibril- $\text{CH}_2\text{OH} + \text{O}(\text{COR-Y})_2 \longrightarrow \text{F-CH}_2\text{OCOR-Y}$

Fibril- $\text{CH}_2\text{OH} + \text{HOOC-R-Y} \longrightarrow \text{F-CH}_2\text{OCOR-Y}$

Fibril- CH_2 -Halogen + $\text{Y}^- \longrightarrow \text{F-CH}_2-\text{Y} + \text{X}^- \quad \text{Y}^- = \text{NCO}^-$, -

40 OR $^-$

Fibril- $\text{C=O} + \text{H}_2\text{N-R-Y} \longrightarrow \text{F-C=N-R-Y}$

Fibrils Functionalized by Adsorption of Polynuclear or Polyheteronuclear Aromatic or Planar Macroyclic Compounds

Dilithium phthalocyanine: In general, the two 5 Li^+ ions are displaced from the phthalocyanine (Pc) group by most metal (particularly multi-valent) complexes. Therefore, displacement of the Li^+ ions with a metal ion bonded with non-labile ligands is a method of putting 10 stable functional groups onto fibril surfaces. Nearly 10 all transition metal complexes will displace Li^+ from Pc to form a stable, non-labile chelate. The point is then to couple this metal with a suitable ligand.

Cobalt (II) Phthalocyanine

Cobalt (II) complexes are particularly suited 15 for this. Co^{++} ion can be substituted for the two Li^+ ions to form a very stable chelate. The Co^{++} ion can then be coordinated to a ligand such as nicotinic acid, which contains a pyridine ring with a pendant carboxylic acid group and which is known to bond preferentially to the 20 pyridine group. In the presence of excess nicotinic acid, $\text{Co}(\text{II})\text{Pc}$ can be electrochemically oxidized to $\text{Co}(\text{III})\text{Pc}$, forming a non-labile complex with the pyridine moiety of nicotinic acid. Thus, the free carboxylic acid group of the nicotinic acid ligand is firmly attached to 25 the fibril surface.

Other suitable ligands are the aminopyridines or ethylenediamine (pendant NH_2), mercaptopyridine (SH), or other polyfunctional ligands containing either an amino- or pyridyl- moiety on one end, and any desirable 30 function on the other.

7. 3-DIMENSIONAL STRUCTURES

The oxidized fibrils are more easily dispersed in aqueous media than unoxidized fibrils. Stable, porous 3-dimensional structures with meso- and macropores (pores 35 >2 nm) are very useful as catalysts or chromatography supports. Since fibrils can be dispersed on an individualized basis, a well-dispersed sample which is

stabilized by cross-links allows one to construct such a support. Functionalized fibrils are ideal for this application since they are easily dispersed in aqueous or polar media and the functionality provides cross-link points. Additionally, the functionality provides points to support the catalytic or chromatographic sites. The end result is a rigid, 3-dimensional structure with its total surface area accessible with functional sites on which to support the active agent.

Typical applications for these supports in catalysis include their use as a highly porous support for metal catalysts laid down by impregnation, e.g., precious metal hydrogenation catalysts. Moreover, the ability to anchor molecular catalysts by tether to the support via the functionality combined with the very high porosity of the structure allows one to carry out homogeneous reactions in a heterogeneous manner. The tethered molecular catalyst is essentially dangling in a continuous liquid phase, similar to a homogeneous reactor, in which it can make use of the advantages in selectivities and rates that go along with homogeneous reactions. However, being tethered to the solid support allows easy separation and recovery of the active, and in many cases, very expensive catalyst.

These stable, rigid structures also permits carrying out heretofore very difficult reactions, such as asymmetric syntheses or affinity chromatography by attaching a suitable enantiomeric catalyst or selective substrate to the support. Derivatization through Metallo-Pc or Metallo-porphyrin complexes also allows for retrieval of the ligand bonded to the metal ion, and furthermore, any molecule which is bonded to the ligand through the secondary derivatives. For example, in the case where the 3-dimensional structure of functionalized fibrils is an electrode, or part of an electrode, and the functionalization has resulted from adsorption of Co(II)Pc, electrochemical oxidation of Co(II) to Co(III)

in the presence of nicotinic acid will produce a non-labile Co(III)-pyridyl complex with a carboxylic acid as the pendent group. Attaching a suitable antigen, antibody, catalytic antibody, or other site-specific trapping agent will permit selective separations of molecules (affinity chromatography) which are otherwise very difficult to achieve. After washing the electrode to remove occluded material, the Co(III) complex containing the target molecule can be electrochemically reduced to recover the labile Co(II) complex. The ligand on Co(II) containing the target molecule can then be recovered by mass action substitution of the labile Co(II) ligand, thereby effecting a separation and recovery of molecules which are otherwise very difficult or expensive to perform (e.g., chiral drugs).

Another example of 3-dimensional structures are fibril-ceramic composites.

EXAMPLE 18

Preparation of Alumina-Fibril Composites (185-02-01)

One g of nitric acid oxidized fibrils (185-01-02) was highly dispersed in 100 cc DI water using an U/S disintegrator. The fibril slurry was heated to 90°C and a solution of 0.04 mol aluminum tributoxide dissolved in 20 cc propanol was slowly added. Reflux was continued for 4 hr, after which the condenser was removed to drive out the alcohol. After 30 min the condenser was put back and the slurry refluxed at 100°C overnight. A black sol with uniform appearance was obtained. The sol was cooled to RT and after one week, a black gel with a smooth surface was formed. The gel was heated at 300°C in air for 12 hr.

The alumina-fibril composites were examined by SEM. Micrographs of cracked surfaces showed a homogeneous dispersion of fibrils in the gel.

EXAMPLE 19Preparation of Silica-Fibril Composites (173-85-03)

Two g of nitric acid oxidized fibrils (173-83-03) were highly dispersed on 200 cc ethanol using ultrasonification. A solution of 0.1 mol tetraethoxysilane dissolved in 50 cc ethanol was slowly added to the slurry at RT, followed by 3 cc conc. HCL. The mixture was heated to 85°C and maintained at that temperature until the volume was reduced to 100 cc. The mixture was cooled and set aside until it formed a black solid gel. The gel was heated at 300°C in air.

The silica-fibril composites were examined by SEM. Micrographs of cracked surfaces showed a homogeneous dispersion of fibrils in the gel.

Similar preparations with other ceramics, such as zirconia, titania, rare earth oxides as well as ternary oxides can be prepared.

As illustrated by the foregoing description and examples, the invention has application in the formulation of a wide variety of functionalized nanotubes.

The terms and expressions which have been employed are used as terms of description and not of limitations, and there is no intention in the use of such terms or expressions of excluding any equivalents of the features shown and described as portions thereof, its being recognized that various modifications are possible within the scope of the invention.

WHAT IS CLAIMED IS:

1. A composition of matter of the formula



wherein the carbon atoms, C_n , are surface
5 carbons of a substantially cylindrical, graphitic
nanotube having a length to diameter ratio of greater
than 5 and a diameter of less than 0.5 micron,

n is an integer, L is a number less than 0.1n,

m is a number less than 0.5n,

10 each of R is the same and is selected from

SO_3H , $COOH$, NH_2 , OH , CHO , CN , $COCl$, halide, $COSH$, SH ,
 $COOR'$, SR' , SiR'_3 , $Si\{OR'\}_yR'^{3-y}$, $Si\{O-SiR'_2\}OR'$, R'' , Li ,
 AlR'_2 , $Hg-X$, TlZ_2 and $Mg-X$, y is an integer equal
to or less than 3,

15 R' is alkyl, aryl, cycloalkyl, aralkyl or
cycloaryl,

R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl
or fluoroaralkyl,

X is a halide, and

20 Z is carboxylate or trifluoroacetate.

2. A composition of matter of the formula



wherein the carbon atoms, C_n , are surface
carbons of a substantially cylindrical, graphitic fibril
25 being substantially free of pyrolytically deposited
carbon, the projection of the graphite layers on said
fibrils extends for a distance of at least two fibril
diameters,

n is an integer, L is a number less than 0.1n,

30 m is a number less than 0.5n,

each of R is the same and is selected from
 SO_3H , $COOH$, NH_2 , OH , CHO , CN , $COCl$, halide, $COSH$, SH ,
 $COOR'$, SR' , SiR'_3 , $Si\{OR'\}_yR'^{3-y}$, $Si\{O-SiR'_2\}OR'$, R'' , Li ,
 AlR'_2 , $Hg-X$, TlZ_2 and $Mg-X$, y is an integer equal
35 to or less than 3,

R' is alkyl, aryl, cycloalkyl, aralkyl or
cycloaryl,

R" is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

X is a halide, and

Z is carboxylate or trifluoroacetate.

5 3. A composition of matter as claimed in claim 2, wherein said fibril comprises cylindrical graphitic sheets whose c-axes are substantially perpendicular to their cylindrical axis.

10 4. A composition of matter as claimed in claim 2, wherein the outer diameter of said fibrils is less than 0.1 micron.

5. A composition of matter of the formula



wherein the carbon atoms, C_n , are surface atoms 15 of a fishbone fibril,

n is an integer, L is a number less than 0.1n,

m is a number less than 0.5n,

each of R is the same and is selected from

SO₃H, COOH, NH₂, OH, CHO, CN, COCl, halide, COSH, SH,

20 COOR', SR', SiR'₃, Si{OR'}_yR'_{3-y}, Si{O-SiR'₂}OR', R", Li, AlR'₂, Hg-X, TlZ₂ and Mg-X, y is an integer equal to or less than 3,

R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

25 R" is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

X is a halide, and

Z is carboxylate or trifluoroacetate.

6. A composition of matter of the formula



30 wherein the carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic nanotube having a length to diameter ratio of greater than 5 and a diameter of less than 0.5 micron,

35 n is an integer, L is a number less than 0.1n and m is a number less than 0.5n,

each of R is selected from SO_3H , COOH , NH_2 , OH , CHO , CN , COCl , halide, COSH , SH , COOR' , SR' , SiR'_3 , $\text{Si}(\text{OR}')_y\text{R}'_{3-y}$, $\text{Si}(\text{O-SiR}'_2)\text{OR}'$, R'' , Li , AlR'_2 , Hg-X , TiZ_2 and Mg-X ,

5 y is an integer equal to or less than 3,
R' is selected from alkyl, aryl, cycloalkyl,
aralkyl, cycloaryl,
R'' is a fluoroalkyl, fluoroaryl,
fluorocycloalkyl or fluoroaralkyl,

10 X is a halide,
Z is carboxylate or trifluoroacetate,
and further provided that where each of R is an
oxygen-containing group COOH is not present.

7. A composition of matter of the formula

15 $[\text{C}_n\text{H}_L]^{\text{R}}\text{R}_m$
wherein the carbon atoms, C_n , are surface
carbons of a substantially cylindrical, graphitic fibril
being substantially free of pyrolytically deposited
carbon, the projection of the graphite layers on said
20 fibrils extends for a distance of at least two fibril
diameters,

n is an integer, L is a number less than 0.1n
and m is a number less than 0.5n,

25 each of R is selected from SO_3H , COOH , NH_2 , OH ,
 CHO , CN , COCl , halide, COSH , SH , COOR' , SR' , SiR'_3 ,
 $\text{Si}(\text{OR}')_y\text{R}'_{3-y}$, $\text{Si}(\text{O-SiR}'_2)\text{OR}'$, R'' , Li , AlR'_2 , Hg-X , TiZ_2
and Mg-X ,

30 y is an integer equal to or less than 3,
R' is alkyl, aryl, cycloalkyl, aralkyl or
cycloaryl,

R'' is a fluoroalkyl, fluoroaryl,
fluorocycloalkyl or fluoroaralkyl,

35 x is a halide,
Z is a carboxylate or trifluoroacetate,
and further provided that where each of R is an
oxygen-containing group COOH is not present.

8. A composition of matter as claimed in claim 7, wherein said fibril comprises cylindrical graphitic sheets whose c-axes are substantially perpendicular to their cylindrical axis.

5 9. A composition of matter as claimed in claim 7, wherein the outer diameter of said fibrils is less than 0.1 micron.

10. A composition of matter of the formula



wherein the carbon atoms, C_n , are surface atoms of a fishbone fibril,

n is an integer, L is a number less than 0.1n and m is a number less than 0.5n,

each of R is selected from SO_3H , $COOH$, NH_2 , OH ,
15 CHO , CN , $COCl$, halide, $COSH$, SH , $COOR'$, SR' , SiR'_3 ,
 $Si(OR')_yR'_{3-y}$, $Si(O-SiR'_2)OR'$, R'' , Li , AlR'_2 , $Hg-X$, TlZ_2
and $Mg-X$,

20 y is an integer equal to or less than 3,
R' is alkyl, aryl, cycloalkyl, aralkyl or
cycloaryl,

R'' is a fluoroalkyl, fluoroaryl,
fluorocycloalkyl or fluoroaralkyl,

X is a halide,

Z is a carboxylate or trifluoroacetate,

25 and further provided that where each of R is an oxygen-containing group $COOH$ is not present.

11. A composition of matter of the formula



wherein the carbon atoms, C_n , are surface 30 carbons of a substantially cylindrical, graphitic nanotube having a length to diameter ratio of greater than 5 and a diameter of less than 0.5 micron,

n is an integer, L is a number less than 0.1n and m is a number less than 0.5n,

35 each of R is selected from SO_3H , $COOH$, NH_2 , OH , CHO , CN , $COCl$, halide, $COSH$, SH , $COOR'$, SR' , SiR'_3 ,

$\text{Si}(\text{OR}')_y\text{R}'_{3-y}$, $\text{Si}(\text{O-SiR}'_2)\text{OR}'$, R'' , Li , AlR'_2 , Hg-X , TiZ_2 and Mg-X ,

y is an integer equal to or less than 3,
 R' is selected from alkyl, aryl, cycloalkyl,

5 aralkyl, cycloaryl,

R'' is a fluoroalkyl, fluoroaryl,
fluorocycloalkyl or fluoroaralkyl,

X is a halide,

Z is carboxylate or trifluoroacetate,

10 and further provided that each of R does not contain oxygen.

12. A composition of matter of the formula

$[\text{C}_n\text{H}_L]^{\frac{1}{2}}\text{R}_m$

wherein the carbon atoms, C_n , are surface

15 carbons of a substantially cylindrical, graphitic fibril being substantially free of pyrolytically deposited carbon, the projection of the graphite layers on said fibrils extends for a distance of at least two fibril diameters,

20 n is an integer, L is a number less than 0.1n and m is a number less than 0.5n,

each of R is selected from SO_3H , COOH , NH_2 , OH , CHO , CN , COCl , halide, COSH , SH , COOR' , SR' , SiR'_3 , $\text{Si}(\text{OR}')_y\text{R}'_{3-y}$, $\text{Si}(\text{O-SiR}'_2)\text{OR}'$, R'' , Li , AlR'_2 , Hg-X , TiZ_2

25 and Mg-X ,

y is an integer equal to or less than 3,
 R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

R'' is a fluoroalkyl, fluoroaryl,

30 fluorocycloalkyl or fluoroaralkyl,

X is a halide,

Z is a carboxylate or trifluoroacetate,

and further provided that each of R does not contain oxygen.

35 13. A composition of matter as claimed in claim 12, wherein said fibril comprises cylindrical

graphitic sheets whose c-axes are substantially perpendicular to their cylindrical axis.

14. A composition of matter as claimed in claim 12, wherein the outer diameter of said fibrils is 5 less than 0.1 micron.

15. A composition of matter of the formula



wherein the carbon atoms, C_n , are surface atoms of a fishbone fibril,

10 n is an integer, L is a number less than 0.1n and m is a number less than 0.5n,

each of R is selected from SO_3H , $COOH$, NH_2 , OH , CHO , CN , $COCl$, halide, $COSH$, SH , $COOR'$, SR' , SiR'_3 , $Si\{OR'\}_yR'^{3-y}$, $Si\{O-SiR'_2\}OR'$, R'' , Li , AlR'_2 , $Hg-X$, TlZ_2

15 and $Mg-X$,

y is an integer equal to or less than 3,
R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

20 R'' is a fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

X is a halide,

Z is a carboxylate or trifluoroacetate,

and further provided that each of R does not contain oxygen.

25 16. A composition of matter of the formula



wherein the carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic nanotube having a length to diameter ratio of greater 30 than 5 and a diameter of less than 0.1 micron,

n is an integer, L is a number less than 0.1n, m is a number less than 0.5n,

each of A is selected from

35 O O O O
| | | |
 OY , NHY , $C-OY$, $C-NR'Y$, $C-SY$, $C-Y$, $-CR'_2-OY$, $N=Y$, and $C=Y$,

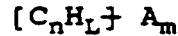
Y is an appropriate functional group of a protein, a peptide, an enzyme, an antibody, a nucleotide, an oligonucleotide, an antigen, or an enzyme substrate, enzyme inhibitor or the transition state analog of an 5 enzyme substrate or is selected from R'-OH, R'-NH₂, R'SH, R'CHO, R'CN, R'X, R'SiR'₃, R'Si \langle OR' \rangle _yR'_{3-y}, R'Si \langle O- SiR'₂ \rangle OR', R'-R'', R'-N-CO, (C₂H₄O \rangle _wH, \langle C₃H₆O \rangle _wH, \langle C₂H₄O \rangle _w- R', (C₃H₆O)_w-R' and R',

10 y is an integer equal to or less than 3,
R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

15 X is a halide,
Z is carboxylate or trifluoroacetate, and
w is an integer greater than one and less than 200.

17. A composition of matter of the formula



20 wherein the carbon atoms, C_n, are surface carbons of a substantially cylindrical, graphitic fibril being substantially free of pyrolytically deposited carbon, the projection of the graphite layers on said fibrils extends for a distance of at least two fibril 25 diameters,

n is an integer, L is a number less than 0.1n, m is a number less than 0.5n,

each of A is selected from

30
$$\begin{array}{c} O & O & O & O \\ || & || & | & | \\ OY, & C-OY, & C-NR'Y, & C-SY, & C-Y, & -CR'_2-OY, & N=Y, & \text{and } C=Y- \end{array}$$

Y is an appropriate functional group of a protein, a peptide, an enzyme, an antibody, a nucleotide, 35 an oligonucleotide, an antigen, or an enzyme substrate, enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from R'-OH, R'-NH₂, R'SH, R'CHO, R'CN, R'X, R'SiR'₃, R'Si \langle OR' \rangle _yR'_{3-y}, R'Si \langle O-

$\text{SiR}'_2\text{OR}'$, $\text{R}'\text{-R}''$, $\text{R}'\text{-N-CO}$, $(\text{C}_2\text{H}_4\text{O})_w\text{H}$, $(\text{C}_3\text{H}_6\text{O})_w\text{H}$, $(\text{C}_2\text{H}_4\text{O})_w\text{-R}'$, $(\text{C}_3\text{H}_6\text{O})_w\text{-R}'$ and R' ,

y is an integer equal to or less than 3,

R' is alkyl, aryl, cycloalkyl, aralkyl or

5. cycloaryl,

R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

X is a halide,

Z is carboxylate or trifluoroacetate, and

10 w is an integer greater than one and less than 200.

18. A composition of matter as claimed in claim 17, wherein said fibril comprises cylindrical graphitic sheets whose c-axes are substantially 15 perpendicular to their cylindrical axis.

19. A composition of matter as claimed in claim 17, wherein the outer diameter of said fibrils is less than 0.1 micron.

20. A composition of matter of the formula $[\text{C}_n\text{H}_L]^{\text{A}}_m$

wherein the carbon atoms, C_n , are surface atoms of a fishbone fibril,

n is an integer, L is a number less than 0.1n, m is a number less than 0.5n,

25 each of A is selected from



30 Y is an appropriate functional group of a protein, a peptide, an enzyme, an antibody, a nucleotide, an oligonucleotide, an antigen, or an enzyme substrate, enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from $\text{R}'\text{-OH}$, $\text{R}'\text{-NH}_2$, $\text{R}'\text{SH}$, $\text{R}'\text{CHO}$, $\text{R}'\text{CN}$, $\text{R}'\text{X}$, $\text{R}'\text{SiR}'_3$, $\text{R}'\text{Si}(\text{OR}')_y\text{R}'_3-y$, $\text{R}'\text{Si}(\text{O-OR}')_2\text{OR}'$, $\text{R}'\text{-R}''$, $\text{R}'\text{-N-CO}$, $(\text{C}_2\text{H}_4\text{O})_w\text{H}$, $(\text{C}_3\text{H}_6\text{O})_w\text{H}$, $(\text{C}_2\text{H}_4\text{O})_w\text{-R}'$, $(\text{C}_3\text{H}_6\text{O})_w\text{-R}'$ and R' ,

y is an integer equal to or less than 3,

R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

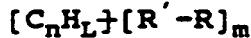
R" is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

5 X is a halide,

Z is carboxylate or trifluoroacetate, and

w is an integer greater than one and less than 200.

21. A composition of matter of the formula



10 wherein the carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic nanotube having a length to diameter ratio of greater than 5 and a diameter of less than 0.5 micron,

15 n is an integer, L is a number less than 0.1n, m is a number less than 0.5n,

each of R is selected from SO_3H , $COOH$, NH_2 , OH , CHO , CN , $COCl$, halide, $COSH$, SH , $COOR'$, SR' , SiR'_3 , $Si\{OR'\}_yR'_{3-y}$, $Si\{O-SiR'\}_2\}OR'$, R'' , Li , AlR'_2 , $Hg-X$, TlZ_2

20 and $Mg-X$,

y is an integer equal to or less than 3,

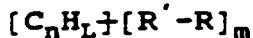
R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

X is a halide,

25 R" is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl, and

Z is carboxylate or trifluoroacetate.

22. A composition of matter of the formula



30 wherein the carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic fibril being substantially free of pyrolytically deposited carbon, the projection of the graphite layers on said fibrils extends for a distance of at least two fibril 35 diameters,

n is an integer, L is a number less than 0.1n,

m is a number less than 0.5n,

each of R is selected from SO_3H , COOH , NH_2 , OH , CHO , CN , COCl , halide, COSH , SH , COOR' , SR' , SiR'_3 , $\text{Si}\{\text{OR}'\}_y\text{R}'_{3-y}$, $\text{Si}\{\text{O-SiR}'_2\}\text{OR}'$, R'' , Li , AlR'_2 , Hg-X , TlZ_2 and Mg-X ,

5 y is an integer equal to or less than 3,
 R' is alkyl, aryl, cycloalkyl, aralkyl or
cycloaryl,

X is a halide,

10 R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl
or fluoroaralkyl, and

Z is carboxylate or trifluoroacetate.

23. A composition of matter as claimed in
claim 22, wherein said fibril comprises cylindrical
graphitic sheets whose c-axes are substantially
15 perpendicular to their cylindrical axis.

24. A composition of matter as claimed in
claim 22, wherein the outer diameter of said fibrils is
less than 0.1 micron.

25. A composition of matter of the formula
20 $[\text{C}_n\text{H}_L\{\text{R}'-\text{R}\}]_m$

wherein the carbon atoms, C_n , are surface atoms
of a fishbone fibril,

n is an integer, L is a number less than 0.1n,
m is a number less than 0.5n,

25 each of R is selected from SO_3H , COOH , NH_2 , OH ,
 CHO , CN , COCl , halide, COSH , SH , COOR' , SR' , SiR'_3 ,
 $\text{Si}\{\text{OR}'\}_y\text{R}'_{3-y}$, $\text{Si}\{\text{O-SiR}'_2\}\text{OR}'$, R'' , Li , AlR'_2 , Hg-X , TlZ_2
and Mg-X ,

30 y is an integer equal to or less than 3,
 R' is alkyl, aryl, cycloalkyl, aralkyl or
cycloaryl,

X is a halide,

35 R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl
or fluoroaralkyl, and

35 Z is carboxylate or trifluoroacetate.

26. A composition of matter of the formula

$[\text{C}_n\text{H}_L\{\text{R}'-\text{A}\}]_m$

wherein the carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic nanotube having a length to diameter ratio of greater than 5 and a diameter of less than 0.5 micron,

5 n is an integer, L is a number less than 0.1n,
m is a number less than 0.5n,

each of R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

A is selected from

10 $\begin{array}{c} O & O & O & O \\ || & | & | & | \\ OY & NHY & C-OY & C-NR'Y & C-SY & C-Y & -CR'_2-OY & N=Y & C=Y \end{array}$

Y is an appropriate functional group of a protein, a peptide, an enzyme, an antibody, a nucleotide, 15 an oligonucleotide, an antigen, or an enzyme substrate, enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from $R'-OH$, $R'-NH_2$, $R'SH$, $R'CHO$, $R'CN$, $R'X$, $R'SiR'_3$, $R'Si\leftarrow OR'\rightleftharpoons R'_3-y$, $R'Si\leftarrow O-SiR'_2\rightleftharpoons OR'$, $R''-R''$, $R''-N-CO$, $(C_2H_4O)_wH$, $\leftarrow C_3H_6O\rightleftharpoons wH$, $\leftarrow C_2H_4O\rightleftharpoons wH$, R' , $(C_3H_6O)_w-R'$ and R' ,

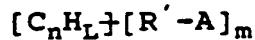
20 y is an integer equal to or less than 3,
 R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

25 X is a halide,

Z is carboxylate or trifluoroacetate, and

w is an integer greater than one and less than 200.

27. A composition of matter of the formula



30 wherein the carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic fibril being substantially free of pyrolytically deposited carbon, the projection of the graphite layers on said fibrils extends for a distance of at least two fibril 35 diameters,

n is an integer, L is a number less than 0.1n,
m is a number less than 0.5n,

each of R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

A is selected from

5 $\begin{array}{c} \text{O} & \text{O} & \text{O} & \text{O} \\ | & | & | & | \\ \text{OY}, \text{NHY}, \text{C}-\text{OY}, \text{C}-\text{NR}'\text{Y}, \text{C}-\text{SY}, \text{C}-\text{Y}, -\text{CR}'_2-\text{CY}, \text{N}=\text{Y}, \text{and C}=\text{Y}, \end{array}$

Y is an appropriate functional group of a protein, a peptide, an enzyme, an antibody, a nucleotide, an oligonucleotide, an antigen, or an enzyme substrate, 10 enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from R'-OH, R'-NH₂, R'SH, R'CHO, R'CN, R'X, R'SiR'₃, R'Si{OR'+}yR'_{3-y}, R'Si{O-SiR'₂}OR', R'-R'', R'-N-CO, (C₂H₄O)_wH, (C₃H₆O)_wH, (C₂H₄O)_w-R', (C₃H₆O)_w-R' and R', 15 y is an integer equal to or less than 3, R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

X is a halide,

Z is carboxylate or trifluoroacetate, and

20 w is an integer greater than one and less than 200.

28. A composition of matter as claimed in claim 27, wherein said fibril comprises cylindrical graphitic sheets whose c-axes are substantially perpendicular to their cylindrical axis.

29. A composition of matter as claimed in claim 27, wherein the outer diameter of said fibrils is less than 0.1 micron.

30. A composition of matter of the formula [C_nH_L]{R'-A}_m

wherein the carbon atoms, C_n, are surface atoms of a fishbone fibril,

n is an integer, L is a number less than 0.1n, m is a number less than 0.5n,

35 each of R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

A is selected from



5 y is an appropriate functional group of a protein, a peptide, an enzyme, an antibody, a nucleotide, an oligonucleotide, an antigen, or an enzyme substrate, enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from R'-OH, R'-NH₂, R'SH, 10 R'CHO, R'CN, R'X, R'SiR'₃, R'Si + OR' \gamma _yR'_{3-y}, R'Si + O-SiR'₂ + OR', R"-R", R"-N-CO, (C₂H₄O)_wH, (C₃H₆O)_wH, (C₂H₄O)_w-R', (C₃H₆O)_w-R' and R',

y is an integer equal to or less than 3,

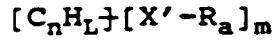
15 R" is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

X is a halide,

Z is carboxylate or trifluoroacetate, and

w is an integer greater than one and less than 200.

20 31. A composition of matter of the formula



wherein the carbon atoms, C_n, are surface carbons of a substantially cylindrical, graphitic nanotube having a length to diameter ratio of greater 25 than 5 and a diameter of less than 0.5 micron,

n is an integer, L is a number less than 0.1n,

m is a number less than 0.5n, a is zero or an integer less than 10,

each of R is selected from SO₃H, COOH, NH₂, OH,

30 CHO, CN, COCl, halide, COSH, SH, COOR', SR', SiR'₃, Si + OR' \gamma _yR'_{3-y}, Si + O-SiR'₂ + OR', R", Li, AlR'₂, Hg-X, TlZ₂ and Mg-X,

y is an integer equal to or less than 3,

R' is alkyl, aryl, cycloalkyl, aralkyl or

35 cycloaryl,

X is a halide,

X' is a polynuclear aromatic, polyheteronuclear aromatic or metallocopolyheteronuclear aromatic moiety,

R" is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl, and

Z is carboxylate or trifluoroacetate.

32. A composition of matter of the formula

5

$$[C_nH_L][X'-R_a]_m$$

wherein the carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic fibril being substantially free of pyrolytically deposited carbon, the projection of the graphite layers on said 10 fibrils extends for a distance of at least two fibril diameters,

n is an integer, L is a number less than 0.1n, m is a number less than 0.5n, a is zero or an integer less than 10,

15 each of R is selected from SO_3H , $COOH$, NH_2 , OH , CHO , CN , $COCl$, halide, $COSH$, SH , $COOR'$, SR' , SiR'_3 , $Si(O-OR')_yR'^{3-y}$, $Si(O-SiR'_2)OR'$, R", Li, AlR'_2 , $Hg-X$, TlZ_2 and $Mg-X$,

20 y is an integer equal to or less than 3,
R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

X is a halide,

X' is a polynuclear aromatic, polyheteronuclear aromatic or metallopoliheteronuclear aromatic moiety,

25 R" is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl, and

Z is carboxylate or trifluoroacetate.

33. A composition of matter as claimed in claim 32, wherein said fibril comprises cylindrical 30 graphitic sheets whose c-axes are substantially perpendicular to their cylindrical axis.

34. A composition of matter as claimed in claim 32, wherein the outer diameter of said fibrils is less than 0.1 micron.

35. A composition of matter of the formula

$$[C_nH_L][X'-R_a]_m$$

wherein the carbon atoms, C_n , are surface atoms of a fishbone fibril,

n is an integer, L is a number less than 0.1n, m is a number less than 0.5n, a is zero or an integer 5 less than 10,

each of R is selected from SO_3H , $COOH$, NH_2 , OH , CHO , CN , $COCl$, halide, $COSH$, SH , $COOR'$, SR' , SiR'_3 , $Si\{OR'\}_yR'^{3-y}$, $Si\{O-SiR'_2\}OR'$, R'' , Li , AlR'_2 , $Hg-X$, TlZ_2 and $Mg-X$,

10 y is an integer equal to or less than 3, R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

X is a halide,

15 X' is a polynuclear aromatic, polyheteronuclear aromatic or metallocopolyheteronuclear aromatic moiety,

R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl, and

Z is carboxylate or trifluoroacetate.

36. A composition of matter of the formula

20 $[C_nH_L]^m[X'^{-}A_a]_m$

wherein the carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic nanotube having a length to diameter ratio of greater than 5 and a diameter of less than 0.5 micron,

25 n is an integer, L is a number less than 0.1n, m is a number less than 0.5n, a is an integer less than 10,

each of A is selected from



Y is an appropriate functional group of a protein, a peptide, an enzyme, an antibody, a nucleotide, an oligonucleotide, an antigen, or an enzyme substrate, enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from R'-OH, R'-NH₂, R'SH, R'CHO, R'CN, R'X, R'SiR'₃, R'Si $\text{+OR'}_y\text{R'}_{3-y}$, R'Si +O- SiR'₂ +OR' , R'-R'', R'-N-CO, (C₂H₄O)_wH, (C₃H₆O)_wH, (C₂H₄O)_w-R', (C₃H₆O)_w-R' and R',

y is an integer equal to or less than 3,

15 R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

X is a halide,

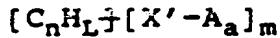
20 X' is a polynuclear aromatic, polyheteronuclear aromatic or metallocopolyheteronuclear aromatic moiety,

Z is carboxylate or trifluoroacetate, and

w is an integer greater than one and less than

200.

25 37. A composition of matter of the formula



wherein the carbon atoms, C_n, are surface carbons of a substantially cylindrical, graphitic fibril being substantially free of pyrolytically deposited carbon, the projection of the graphite layers on said fibrils extends for a distance of at least two fibril diameters,

n is an integer, L is a number less than 0.1n,

m is a number less than 0.5n, a is an integer less than

35 10,

each of A is selected from



5 Y is an appropriate functional group of a protein, a peptide, an enzyme, an antibody, a nucleotide, an oligonucleotide, an antigen, or an enzyme substrate, enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from R'-OH, R'-NH₂, R'SH,

10 R'CHO, R'CN, R'X, R'SiR'₃, R'Si + OR' - yR'_{3-y}, R'Si + O-SiR'₂ + OR', R'-R", R'-N-CO, (C₂H₄O)_wH, (C₃H₆O)_wH, (C₂H₄O)_w-R', (C₃H₆O)_w-R' and R',

y is an integer equal to or less than 3,

R' is alkyl, aryl, cycloalkyl, aralkyl or 15 cycloaryl,

R" is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

X is a halide,

20 X' is a polynuclear aromatic, polyheteronuclear aromatic or metallocopolyheteronuclear aromatic moiety,

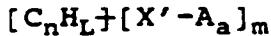
Z is carboxylate or trifluoroacetate, and

w is an integer greater than one and less than 200.

38. A composition of matter as claimed in 25 claim 37, wherein said fibril comprises cylindrical graphitic sheets whose c-axes are substantially perpendicular to their cylindrical axis.

39. A composition of matter as claimed in claim 37, wherein the outer diameter of said fibrils is 30 less than 0.1 micron.

40. A composition of matter of the formula



wherein the carbon atoms, C_n, are surface atoms of a fishbone fibril,

35 n is an integer, L is a number less than 0.1n, m is a number less than 0.5n, a is an integer less than 10,

each of A is selected from

$\begin{array}{c} \text{O} & \text{O} & \text{O} & \text{O} \\ | & | & | & | \\ \text{OY, NHY, C-OY, C-NR'Y, C-SY, C-Y, -CR'}_2\text{-OY, N=Y, and C=Y,} \\ \text{Y is an appropriate functional group of a} \\ \text{5 protein, a peptide, an enzyme, an antibody, a nucleotide,} \\ \text{an oligonucleotide, an antigen, or an enzyme substrate,} \\ \text{enzyme inhibitor or the transition state analog of an} \\ \text{enzyme substrate or is selected from R'-OH, R'-NH}_2, \text{R'SH,} \\ \text{R'CHO, R'CN, R'X, R'SiR'}_3, \text{R'Si}(\text{OR'})_y\text{R'}_{3-y}, \text{R'Si}(\text{O-}) \\ \text{10 SiR'}_2\text{)OR', R'-R'', R'-N-CO, (C}_2\text{H}_4\text{O)}_w\text{H, (C}_3\text{H}_6\text{O)}_w\text{H, (C}_2\text{H}_4\text{O)}_w\text{-} \\ \text{R', (C}_3\text{H}_6\text{O)}_w\text{-R' and R',} \\ \text{y is an integer equal to or less than 3,} \\ \text{R' is alkyl, aryl, cycloalkyl, aralkyl or} \\ \text{cycloaryl,} \\ \text{15 R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl} \\ \text{or fluoroaralkyl,} \\ \text{X is a halide,} \\ \text{X' is a polynuclear aromatic, polyheteronuclear} \\ \text{aromatic or metallopolyyheteronuclear aromatic moiety,} \\ \text{20 Z is carboxylate or trifluoroacetate, and} \\ \text{w is an integer greater than one and less than} \\ \text{200.} \end{array}$

41. A composition of matter as claimed in
claims 31-40, wherein X' is a phthalocyanine or
25 porphyrin.

42. A method of forming a composition of
matter of the formula



wherein the carbon atoms, C_n , are surface
30 carbons of a substantially cylindrical, graphitic
nanotube,

n is an integer, L is a number less than 0.1n,
m is a number less than 0.5n,
each of R is the same and is selected from
35 SO_3H , COOH , NH_2 , OH , CHO , CN , COCl , halide, COSH , SH ,
 COOR' , SR' , SiR'_3 , $\text{Si}(\text{OR'})_y\text{R'}_{3-y}$, $\text{Si}(\text{O-SiR'}_2\text{)OR'}$, R'' , Li ,
 AlR'_2 , Hg-X , TlZ_2 and Mg-X , y is an integer equal
to or less than 3,

R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

R" is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

5 X is a halide, and

Z is carboxylate or trifluoroacetate,

comprising the step of reacting the surface carbons with an appropriate reagent under conditions sufficient to form functionalized nanotubes having the

10 formula $[C_nH_L]R_m$.

43. A method of forming a composition of matter of the formula



wherein the carbon atoms, C_n , are surface 15 carbons of a substantially cylindrical, graphitic nanotube,

n is an integer, L is a number less than 0.1n and m is a number less than 0.5n,

each of R is selected from SO_3H , $COOH$, NH_2 , OH , 20 CHO , CN , $COCl$, halide, $COSH$, SH , $COOR'$, SR' , SiR'_3 , $Si\{OR'\}_yR'^{3-y}$, $Si\{O-SiR'\}_2\}OR'$, R'' , Li , AlR'_2 , $Hg-X$, TlZ_2 and $Mg-X$,

y is an integer equal to or less than 3,

R' is selected from alkyl, aryl, cycloalkyl,

25 aralkyl, cycloaryl,

R" is a fluoroalkyl, fluoroaryl,

fluorocycloalkyl or fluoroaralkyl,

X is a halide,

Z is carboxylate or trifluoroacetate,

30 and further provided that where each of R is an oxygen-containing group $COOH$ is not present,

comprising the step of reacting the surface carbons with at least one appropriate reagent under conditions sufficient to form functionalized nanotubes

35 having the formula $[C_nH_L]R_m$.

44. A method of forming a composition of matter of the formula

$$[C_nH_L]_jR_m$$

wherein the carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic nanotube,

5 n is an integer, L is a number less than 0.1n and m is a number less than 0.5n,

each of R is selected from SO_3H , $COOH$, NH_2 , OH , CHO , CN , $COCl$, halide, $COSH$, SH , $COOR'$, SR' , SiR'_3 , $Si\{OR'\}_yR'^{3-y}$, $Si\{O-SiR'_2\}OR'$, R'' , Li , AlR'_2 , $Hg-X$, TlZ_2

10 and $Mg-X$,

y is an integer equal to or less than 3,

R' is selected from alkyl, aryl, cycloalkyl, aralkyl, cycloaryl,

R'' is a fluoroalkyl, fluoroaryl,

15 fluorocycloalkyl or fluoroaralkyl,

X is a halide,

Z is carboxylate or trifluoroacetate,

and further provided that each of R does not contain oxygen,

20 comprising the step of reacting the surface carbons with at least one appropriate reagent under conditions sufficient to form functionalized nanotubes having the formula $[C_nH_L]_jR_m$.

45. A method of forming a composition of
25 matter of the formula

$$[C_nH_L]_jA_m$$

wherein the carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic nanotube,

30 n is an integer, L is a number less than 0.1n, m is a number less than 0.5n,

each of A is selected from



35 and $C=Y$,

Y is an appropriate functional group of a protein, a peptide, an enzyme, an antibody, an

oligonucleotide, a nucleotide, an antigen, or an enzyme substrate, enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from R'-OH, R'-NH₂, R'SH, R'CHO, R'CN, R'X, R'SiR'₃, R'-R'', R'-N-
5 CO, (C₂H₄O)_wH, (C₃H₆O)_wH, (C₂H₄O)_w-R', (C₃H₆O)_w-R' and R',
R' is alkyl, aryl, cycloalkyl, aralkyl or
cycloaryl,
R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl
or fluoroaralkyl,
10 X is a halide,
Z is carboxylate or trifluoroacetate, and
w is an integer greater than one and less than
200,
comprising the steps of:
15 (a) reacting the surface carbons with at least
one appropriate reagent under conditions
sufficient to form substituted nanotubes
having the formula [C_nH_L]_yR_m, wherein each
of R is the same and is selected from
SO₃H, COOH, NH₂, OH, CHO, CN, COCl, halide,
20 COSH, SH, COOR', SR', SiR'₃, Si-OR'_yR'_{3-y},
Si-O-SiR'₂-OR', R'', Li, AlR'₂, Hg-X, TlZ₂
and Mg-X, and y is an integer equal to or
less than 3; and
25 (b) reacting the substituted nanotubes [C_nH_L]_yR_m
with at least one appropriate reagent
under conditions sufficient to form
functionalized nanotubes having the
formula [C_nH_L]_yA_m.
30 46. A method of forming a composition of
matter of the formula



wherein the carbon atoms, C_n, are surface
carbons of a substantially cylindrical, graphitic
35 nanotube having a length to diameter ratio of greater
than 5 and a diameter of less than 0.1 micron,

n is an integer, L is a number less than 0.1n,
m is a number less than 0.5n,
each of A is selected from

5 O O O O
 OY , NHY , $C-OY$, $C-NR'Y$, $C-SY$, $C-Y$, $-CR'_2-OY$, $N=Y$, and
 $C=Y$,

γ is an appropriate functional group of a
 10 protein, a peptide, an enzyme, an antibody, an oligonucleotide, a nucleotide, an antigen, or an enzyme substrate, enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from $R'-OH$, $R'-NH_2$, $R'SH$, $R'CHO$, $R'CN$, $R'X$, $R'SiR'_3$, $R'-R''$, $R'-N-CO$,
 15 $(C_2H_4O)_wH$, $(C_3H_6O)_wH$, $(C_2H_4O)_w-R'$, $(C_3H_6O)_w-R'$ and R' ,
 R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl.

R" is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

20 x is a halide,
 z is carboxylate or trifluoroacetate, and
 w is an integer greater than one and less than
200.

comprising the steps of:

25 (a) reacting the surface carbons with at least one appropriate reagent under conditions sufficient to form substituted nanotubes having the formula $[C_nH_L]_xR_m$, wherein each of R is selected from SO_3H , $COOH$, NH_2 , OH , CHO , CN , $COCl$, halide, $COSH$, SH , $COOR'$, SR' , SiR'_3 , $Si\{OR'\}_yR''_{3-y}$, $Si\{O-SiR'_2\}OR'$, R'' , Li , AlR'_2 , $Hg-X$, TlZ_2 and $Mg-X$, and y is an integer equal to or less than 3; and

30 (b) reacting the substituted nanotubes $[C_nH_L]_xR_m$ with at least one appropriate reagent under conditions sufficient to form functionalized nanotubes having the formula $[C_nH_L]_xA_m$.

35

47. A method of forming a composition of matter of the formula



wherein the carbon atoms, C_n , are surface 5 carbons of a substantially cylindrical, graphitic nanotube being substantially free of pyrolytically deposited carbon,

n is an integer, L is a number less than 0.1n, m is a number less than 0.5n,

10 each of A is selected from



15 Y is an appropriate functional group of a $C=Y$, $N=Y$, and

15 Y is an appropriate functional group of a protein, a peptide, an enzyme, an antibody, an oligonucleotide, a nucleotide, an antigen, or an enzyme substrate, enzyme inhibitor or the transition state

20 analog of an enzyme substrate or is selected from $R'-OH$, $R'-NH_2$, $R'SH$, $R'CHO$, $R'CN$, $R'X$, $R'SiR'_3$, $R'-R''$, $R'-N-CO$, $(C_2H_4O)_wH$, $(C_3H_6O)_wH$, $(C_2H_4O)_w-R'$, $(C_3H_6O)_w-R'$ and R' ,

R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

25 R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

X is a halide,

Z is carboxylate or trifluoroacetate, and

w is an integer greater than one and less than

30 200,

comprising the steps of:

(a) reacting the surface carbons with at least one appropriate reagent under conditions sufficient to form substituted nanotubes 35 having the formula $[C_nH_L]^+ R_m$, wherein each of R is selected from SO_3H , $COOH$, NH_2 , OH , CHO , CN , $COCl$, halide, $COSH$, SH , $COOR'$, SR' , SiR'_3 , $Si\{OR'\}_yR'^{3-y}$, $Si\{O-SiR'_2\}OR'$,

R'', Li, AlR'₂, Hg-X, TlZ₂ and Mg-X, and y is an integer equal to or less than 3; and

(b) reacting the substituted nanotubes $[C_nH_L]R_m$ with at least one appropriate reagent under conditions sufficient to form functionalized nanotubes having the formula $[C_nH_L]A_m$.

48. A method of forming a composition of matter of the formula

10 $[C_nH_L]A_m$

wherein the carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic nanotube,

15 n is an integer, L is a number less than 0.1n, m is a number less than 0.5n,

each of A is selected from



20 OY, NHY, C-OY, C-NR'Y, C-SY, C-Y, -CR'₂-OY, N=Y, and C=Y,

Y is an appropriate functional group of a protein, a peptide, an enzyme, an antibody, an oligonucleotide, a nucleotide, an antigen, or an enzyme 25 substrate, enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from R'-OH, R'-NH₂, R'SH, R'CHO, R'CN, R'X, R'SiR'₃, R'-R'', R'-N-CO, $(C_2H_4O)_wH$, $\{C_3H_6O\}_wH$, $\{C_2H_4O\}_wR'$, $(C_3H_6O)_wR'$ and R', R' is alkyl, aryl, cycloalkyl, aralkyl or

30 cycloaryl,

R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

X is a halide,

Z is carboxylate or trifluoroacetate, and

35 w is an integer greater than one and less than 200,

comprising the step of reacting substituted nanotubes $[C_nH_L]R_m$ with at least one appropriate reagent under conditions sufficient to form functionalized

nanotubes having the formula $[C_nH_L]A_m$, where each of R is the same and is selected from SO_3H , $COOH$, NH_2 , OH , CHO , CN , $COCl$, halide, $COSH$, SH , $COOR'$, SR' , SiR'_3 , $Si\{OR'\}_yR'^{3-y}$, $Si\{O-SiR'_2\}OR'$, R'' , Li , AlR'_2 , $Hg-X$, TlZ_2 and $Mg-X$, and y is an integer equal to or less than 3.

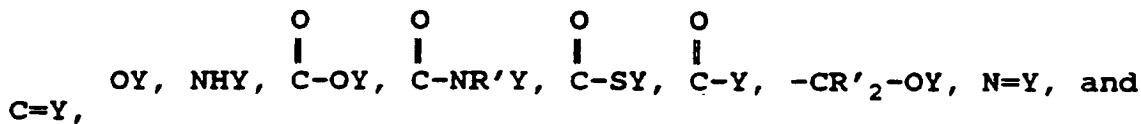
49. A method of forming a composition of matter of the formula



wherein the carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic nanotube having a length to diameter ratio of greater than 5 and a diameter of less than 0.1 micron,

n is an integer, L is a number less than 0.1n, m is a number less than 0.5n,

each of A is selected from



Y is an appropriate functional group of a protein, a peptide, an enzyme, an antibody, an oligonucleotide, a nucleotide, an antigen, or an enzyme substrate, enzyme inhibitor or the transition state

analog of an enzyme substrate or is selected from $R'-OH$, $R'-NH_2$, $R'SH$, $R'CHO$, $R'CN$, $R'X$, $R'SiR'_3$, $R'-R''$, $R'-N-CO$, $(C_2H_4O)_wH$, $(C_3H_6O)_wH$, $(C_2H_4O)_w-R'$, $(C_3H_6O)_w-R'$ and R' , R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

X is a halide,

Z is carboxylate or trifluoroacetate, and

w is an integer greater than one and less than

200,

comprising the step of reacting substituted nanotubes $[C_nH_L]R_m$ with at least one appropriate reagent under conditions sufficient to form functionalized nanotubes having the formula $[C_nH_L]A_m$, where each of R is

selected from SO_3H , COOH , NH_2 , OH , CHO , CN , COCl , halide, COSH , SH , COOR' , SR' , SiR'_3 , $\text{Si}(\text{OR}')_y\text{R}'_{3-y}$, $\text{Si}(\text{O-})\text{SiR}'_2\text{OR}'$, R'' , Li , AlR'_2 , Hg-X , TlZ_2 and Mg-X , and y is an integer equal to or less than 3.

5 50. A method of forming a composition of matter of the formula



wherein the carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic 10 nanotube being substantially free of pyrolytically deposited carbon,

n is an integer, L is a number less than $0.1n$, m is a number less than $0.5n$,

each of A is selected from

15 $\begin{array}{c} \text{O} \\ | \\ \text{OY} \end{array}$, $\begin{array}{c} \text{O} \\ | \\ \text{NHY} \end{array}$, $\begin{array}{c} \text{O} \\ | \\ \text{C-OY} \end{array}$, $\begin{array}{c} \text{O} \\ | \\ \text{C-NR}'\text{Y} \end{array}$, $\begin{array}{c} \text{O} \\ | \\ \text{C-SY} \end{array}$, $\begin{array}{c} \text{O} \\ | \\ \text{C-Y} \end{array}$, $-\text{CR}'_2\text{-OY}$, $\text{N}=\text{Y}$, and $\text{C}=\text{Y}$,

20 Y is an appropriate functional group of a protein, a peptide, an enzyme, an antibody, an oligonucleotide, a nucleotide, an antigen, or an enzyme substrate, enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from $\text{R}'\text{-OH}$, $\text{R}'\text{-NH}_2$, $\text{R}'\text{SH}$, $\text{R}'\text{CHO}$, $\text{R}'\text{CN}$, $\text{R}'\text{X}$, $\text{R}'\text{SiR}'_3$, $\text{R}'\text{-R}''$, $\text{R}'\text{-N-CO-}$, $(\text{C}_2\text{H}_4\text{O})_w\text{H}$, $(\text{C}_3\text{H}_6\text{O})_w\text{H}$, $(\text{C}_2\text{H}_4\text{O})_w\text{-R}'$, $(\text{C}_3\text{H}_6\text{O})_w\text{-R}'$ and R' , R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

25 R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

X is a halide,

Z is carboxylate or trifluoroacetate, and

w is an integer greater than one and less than

30 200,

35 comprising the step of reacting substituted nanotubes $[\text{C}_n\text{H}_L]^{\frac{1}{2}}\text{R}_m$ with at least one appropriate reagent under conditions sufficient to form functionalized nanotubes having the formula $[\text{C}_n\text{H}_L]^{\frac{1}{2}}\text{A}_m$, where each of R is selected from SO_3H , COOH , NH_2 , OH , CHO , CN , COCl , halide,

COSH, SH, COOR', SR', SiR'₃, Si-OR'_yR'_{3-y}, Si-O-SiR'₂-OR', R'', Li, AlR'₂, Hg-X, TlZ₂ and Mg-X, and y is an integer equal to or less than 3.

51. A method of forming a composition of matter of the formula



wherein the carbon atoms, C_n, are surface carbons of a substantially cylindrical, graphitic nanotube,

10 n is an integer, L is a number less than 0.1n, m is a number less than 0.5n,

each of R is selected from SO₃H, COOH, NH₂, OH, CHO, CN, COCl, halide, COSH, SH, COOR', SR', SiR'₃, Si-OR'_yR'_{3-y}, Si-O-SiR'₂-OR', R'', Li, AlR'₂, Hg-X, TlZ₂ 15 and Mg-X,

y is an integer equal to or less than 3, R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

X is a halide,

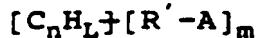
20 R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl, and

Z is carboxylate or trifluoroacetate, comprising the steps of:

25 (a) deoxygenating the graphitic nanotubes under conditions sufficient to form deoxygenated nanotubes; and

(b) reacting the deoxygenated nanotubes with at least one appropriate activated olefin under conditions sufficient to form 30 functionalized nanotubes having the formula [C_nH_L][R'-R]_m.

52. A method of forming a composition of matter of the formula



35 wherein the carbon atoms, C_n, are surface carbons of a substantially cylindrical, graphitic nanotube,

n is an integer, L is a number less than 0.1n,
 m is a number less than 0.5n,

R' is alkyl, aryl, cycloalkyl, aralkyl or
 cycloaryl,

5 x is a halide,

each of A is selected from

O O O O
 | | | |
 OY, NH₂, C-OY, C-NR'Y, C-SY, C-Y, -CR'₂-OY, N=Y, and C=Y,

10 Y is an appropriate functional group of a
 protein, a peptide, an enzyme, an antibody, an
 oligonucleotide, a nucleotide, an antigen, or an enzyme
 substrate, enzyme inhibitor or the transition state
 analog of an enzyme substrate or is selected from R'-OH,
 15 R'-NH₂, R'SH, R'CHO, R'CN, R'X, R'SiR'₃, R'-R", R'-N-CO,
 (C₂H₄O)_wH, (C₃H₆O)_wH, (C₂H₄O)_w-R', (C₃H₆O)_w-R' and R',
 R" is fluoroalkyl, fluoroaryl, fluorocycloalkyl
 or fluoroaralkyl, and

20 Z is carboxylate or trifluoroacetate,
 comprising the steps of:

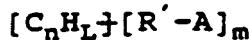
(a) deoxygenating the graphitic nanotubes
 under conditions sufficient to form
 deoxygenated nanotubes;

25 (b) reacting the deoxygenated nanotubes with
 at least one appropriate activated olefin
 to form substituted nanotubes having the
 formula [C_nH_L][R'-R]_m, where each of R is
 selected from SO₃H, COOH, NH₂, OH, CHO, CN,
 COCl, halide, COSH, SH, COOR', SR', SiR'₃,
 Si_yOR'_{3-y},

30 Si_yO-SiR'₂OR', R", Li, AlR'₂, Hg-X, TlZ₂
 and Mg-X, and y is an integer equal to
 or less than 3; and

35 (c) reacting the substituted nanotubes having
 the formula [C_nH_L][R'-R]_m with at least one
 appropriate reagent under conditions
 sufficient to form functionalized
 nanotubes having the formula [C_nH_L][R'-A]_m.

53. A method of forming a composition of matter of the formula



wherein the carbon atoms, C_n , are surface 5 carbons of a substantially cylindrical, graphitic nanotube,

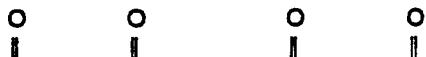
n is an integer, L is a number less than 0.1n,

m is a number less than 0.5n,

10 R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

X is a halide,

each of A is selected from



15 $N=Y$, NHY , $C-OY$, $C-NR'Y$, $C-SY$, $C-Y$, $-CR'_2-OY$, $N=Y$, and $C=Y$,

Y is an appropriate functional group of a protein, a peptide, an enzyme, an antibody, an oligonucleotide, a nucleotide, an antigen, or an enzyme substrate, enzyme inhibitor or the transition state

20 analog of an enzyme substrate or is selected from $R'-OH$, $R'-NH_2$, $R'SH$, $R'CHO$, $R'CN$, $R'X$, $R'SiR'_3$, $R'-R''$, $R'-N-CO$, $(C_2H_4O)_wH$, $(C_3H_6O)_wH$, $(C_2H_4O)_w-R'$, $(C_3H_6O)_w-R'$ and R' ,

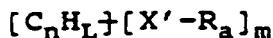
R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl, and

25 Z is carboxylate or trifluoroacetate,

comprising the step of reacting substituted nanotubes having the formula $[C_nH_L][R'-R]_m$ with at least one appropriate reagent under conditions sufficient to form functionalized nanotubes having the formula

30 $[C_nH_L][R'-A]_m$, where each of R is selected from SO_3H , $COOH$, NH_2 , OH , CHO , CN , $COCl$, halide, $COSH$, SH , $COOR'$, SR' , SiR'_3 , $Si\{OR'\}_yR'^{3-y}$, $Si\{O-SiR'_2\}OR'$, R'' , Li , AlR'_2 , $Hg-X$, TlZ_2 and $Mg-X$, and y is an integer equal to or less than 3.

35 54. A method of forming a composition of matter of the formula



wherein the carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic nanotube,

5 n is an integer, L is a number less than 0.1n, m is a number less than 0.5n, a is zero or an integer less than 10,

10 each of R is selected from SO_3H , $COOH$, NH_2 , OH , CHO , CN , $COCl$, halide, $COSH$, SH , $COOR'$, SR' , SiR'_3 , $Si(OR')_yR'^{3-y}$, $Si(O-SiR'_2)OR'$, R'' , Li , AlR'_2 , $Hg-X$, TlZ_2 and $Mg-X$,

15 y is an integer equal to or less than 3, R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

X is a halide,

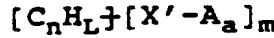
20 X' is a polynuclear aromatic, polyheteronuclear aromatic or metallocopolyheteronuclear aromatic moiety,

R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl, and

25 Z is carboxylate or trifluoroacetate,

comprising the step of adsorbing at least one appropriate macrocyclic compound onto the surface of the graphitic nanotube under conditions sufficient to form a functionalized nanotube having the formula $[C_nH_L][X'-R_a]_m$.

55. A method of forming a composition of matter of the formula



wherein the carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic nanotube,

30 n is an integer, L is a number less than 0.1n, m is a number less than 0.5n, a is an integer less than 10,

35 each of A is selected from

O O O O
 $||$ $||$ $||$ $||$
 OY , NHY , $C-OY$, $C-NR'Y$, $C-SY$, $C-Y$, $-CR'_2-OY$, $N=Y$, and $C=Y$,

Y is an appropriate functional group of a protein, a peptide, an enzyme, an antibody, an

oligonucleotide, a nucleotide, an antigen, or an enzyme substrate, enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from R'-OH, R'-NH₂, R'SH, R'CHO, R'CN, R'X, R'SiR'₃, R'-R'', R'-N-CO, 5 (C₂H₄O)_wH, (C₃H₆O)_wH, (C₂H₄O)_w-R', (C₃H₆O)_w-R' and R', R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl, R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

X is a halide,

10 X' is a polynuclear aromatic, polyheteronuclear aromatic or metallocopolyheteronuclear aromatic moiety,

Z is carboxylate or trifluoroacetate, and

w is an integer greater than one and less than 200,

15 comprising the steps of:

(a) adsorbing at least one appropriate macrocyclic compound onto the surface of the graphitic nanotube under conditions sufficient to form a substituted nanotube having the formula [C_nH_L][X'-R_a]_m, where each of R is selected from SO₃H, COOH, NH₂, OH, CHO, CN, COCl, halide, COSH, SH, COOR', SR', SiR'₃, Si(OR')_yR'_{3-y}, Si(OR'₂)₂GR', R'', Li, AlR'₂, Hg-X, TlZ₂ and 20 Mg-X, and y is an integer equal to or less than 3; and

25 (b) reacting the substituted nanotubes [C_nH_L][X'-R_a]_m with at least one appropriate reagent under conditions sufficient to form a functionalized nanotube having the formula [C_nH_L][X'-A_a]_m.

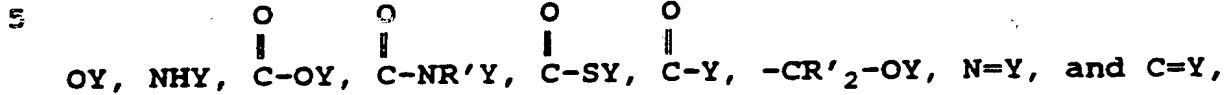
30 56. A method of forming a composition of matter of the formula



35 wherein the carbon atoms, C_n, are surface carbons of a substantially cylindrical, graphitic nanotube,

wherein n is an integer, L is a number less than 0.1n, m is a number less than 0.5n, a is an integer less than 10,

each of A is selected from



Y is an appropriate functional group of a protein, a peptide, an enzyme, an antibody, an 10 oligonucleotide, a nucleotide, an antigen, or an enzyme substrate, enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from R'-OH, R'-NH₂, R'SH, R'CHO, R'CN, R'X, R'SiR'₃, R'-R'', R'-N-CO, (C₂H₄O)_wH, (C₃H₆O)_wH, (C₂H₄O)_w-R', (C₃H₆O)_w-R' and R', 15 R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

X is a halide,

20 X' is a polynuclear aromatic, polyheteronuclear aromatic or metallocopolyheteronuclear aromatic moiety,

Z is carboxylate or trifluoroacetate, and

w is an integer greater than one and less than 200,

25 comprising the step of reacting the substituted nanotubes [C_nH_L][X'-R_a]_m with at least one appropriate reagent under conditions sufficient to form a functionalized nanotube having the formula [C_nH_L][X'-A_a]_m, where each of R is selected from SO₃H, COOH, NH₂, OH, CHO, 30 CN, COCl, halide, COSH, SH, COOR', SR', SiR'₃, Si{OR'}_yR'_{3-y}, Si{O-SiR'₂}OR', R'', Li, AlR'₂, Hg-X, TlZ₂ and Mg-X, and y is an integer equal to or less than 3.

57. A method as recited in claims 54 or 55, wherein prior to the step of adsorbing onto the surface 35 carbons, the graphitic nanotubes are dispersed in a medium.

58. A method as recited in claims 42, 43, 44, 45, 46 or 47, wherein prior to the step of reacting the

surface carbons, the graphitic nanotubes are dispersed in a medium.

59. A method as recited in claims 45, 46, 47, 48, 49, 50, 52, 53, 55 or 56, wherein prior to the step of reacting the substituted nanotubes with the reagent, the substituted nanotubes are dispersed in a medium.

60. A method as recited in claims 42, 43, 44, 45, 46 or 47, wherein the step of reacting the surface carbons comprises sulfonating the surface carbons.

10 61. A method as recited in claims 42, 43, 44, 45, 46, 47, 48, 49 or 50, wherein the step of reacting the surface carbons comprises metallizing the surface carbons with an organometallic reagent.

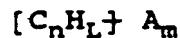
15 62. The method as recited in claims 47 or 50, wherein the projection of the graphite layers on said nanotubes extends for a distance of at least two nanotube diameters.

20 63. The method as recited in claims 47 or 50, wherein said nanotube comprises cylindrical graphitic sheets whose c-axes are substantially perpendicular to their cylindrical axis.

64. The method as recited in claims 47 or 50, wherein the outer diameter of said nanotubes is less than 0.1. micron.

25 65. The method as recited in claims 47 or 50, wherein the carbon atoms, C_n , are surface atoms of a fishbone fibril.

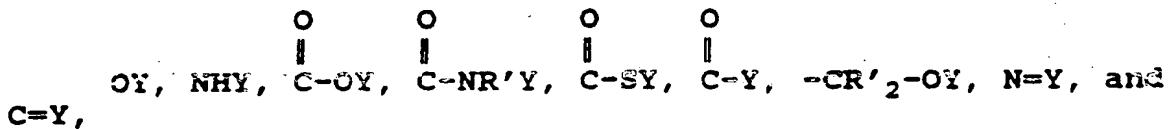
30 66. A method of introducing functional groups onto the surface of carbon nanotubes to form a functionalized nanotube having the formula



wherein the carbon atoms, C_n , are surface carbons of a substantially cylindrical, graphitic nanotube being substantially free of pyrolytically deposited carbon,

n is an integer, L is a number less than 0.1n,
m is a number less than 0.5n,
each of A is selected from

5



Y is an appropriate functional group of a
 10 protein, a peptide, an enzyme, an antibody, an oligonucleotide, a nucleotide, an antigen, or an enzyme substrate, enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from R'-OH, R'-NH₂, R'SH, R'CHO, R'CN, R'X, R'SiR'₃, R'-R", R'-N-CO,
 15 (C₂H₄O)_wH, (C₃H₆O)_wH, (C₂H₄O)_w-R', (C₃H₆O)_w-R' and R',
 R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl.

R" is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

20

x is a halide,

Z is carboxylate or trifluoroacetate, and

w is an integer greater than one and less than 200.

comprising the steps of:

25

(a) contacting the carbon fibrils with oxidizing agents selected from the group including a solution of an alkali metal chlorate in a strong acid for a period of time sufficient to oxidize the surface of said fibrils; and

30

(b) contacting the surface-oxidized carbon fibrils with reactant suitable for adding a functional group to the surface of the carbon fibrils.

36

67. A method as recited in claim 66, wherein the carbon fibrils are subjected to processing prior to contact with the oxidizing agents.

68. A method as recited in claim 66, wherein the processing comprises dispersing the carbon fibrils in a solvent.

5 69. A method as recited in claim 68, wherein after being dispersed in the solvent the carbon fibrils are filtered and dried.

70. A method as recited in claim 66, wherein the alkali metal chlorate is sodium chlorate or potassium chlorate.

10 71. A method as recited in claim 66, wherein the strong acid is sulfuric acid.

72. A method as recited in claim 66, wherein the functional group added to the surface-oxidized fibrils is alkyl/aryl silane.

15 73. A method as recited in claim 66, wherein the functional group added to the surface-oxidized fibrils is a long chain alkyl/aralkyl group.

74. A method as recited in claim 66, wherein the functional group added to the surface-oxidized 20 fibrils is a long chain hydroxyl group.

75. A method as recited in claim 66, wherein the functional group added to the surface-oxidized fibrils is a long chain amine group.

76. A method as recited in claim 66, wherein 25 the functional group added to the surface-oxidized fibrils is a fluorocarbon.

77. A method as recited in claim 66, wherein the time sufficient for oxidization is between about 0.5 hour and 24 hours.

78. A network of functionalized fibrils comprising at least two functionalized fibrils linked at functional groups by either one or more direct bonds or at least one linker moiety, wherein said linker moiety is 5 either bifunctional or polyfunctional.

79. A composition of matter of the formula

[F.F. + linker + F.F.]

wherein the linker is a bifunctional or polyfunctional moiety linked to an appropriate 10 functionalized fibril, [F.F.], derived from the following substituted fibrils:

- (i) $[C_nH_L + R_m]$;
- (ii) $[C_nH_L + R_m]$;
- (iii) $[C_nH_L + A_m]$;
- 15 (iv) $[C_nH_L + [R' - R]_m]$;
- (v) $[C_nH_L + [R' - A]_m]$;
- (vi) $[C_nH_L + [X' - R_a]_m]$; and
- (vii) $[C_nH_L + [X' - A_a]_m]$;

where the carbon atoms, C_n , are surface carbons 20 of a graphitic nanotube,

n is an integer, L is a number less than 0.1n and m is a number less than 0.5n, a is zero or an integer less than 10,

each of R is selected from SO_3H , $COOH$, NH_2 , OH , 25 CHO , CN , $COCl$, halide, $COSH$, SH , $COOR'$, SR' , SiR'_3 , $Si(O-OR')_yR'^{3-y}$, $Si(O-SiR'_2)OR'$, R'' , Li , AlR'_2 , $Hg-X$, TlZ_2 and $Mg-X$,

y is an integer equal to or less than 3,

A is selected from

30
$$\begin{array}{c} O & O & O & O \\ || & || & || & || \\ OY & NHY & C-OY & C-NR'Y & C-SY & C-Y & -CR'_2-OY & N=Y & C=Y \end{array}$$

Y is an appropriate functional group of a protein, a peptide, an enzyme, an antibody, an 35 oligonucleotide, a nucleotide, an antigen, or an enzyme substrate, enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from $R'-OH$,

R'-NH₂, R'SH, R'CHO, R'CN, R'X, R'SiR'₃, R'-R'', R'-N-CO, (C₂H₄O)_wH, (C₃H₆O)_wH, (C₂H₄O)_w-R', (C₃H₆O)_w-R' and R', R' is alkyl, aryl, cycloalkyl, aralkyl or cycloaryl,

5 R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl or fluoroaralkyl,

X is a halide,

X' is a polynuclear aromatic, polyheteronuclear aromatic or metallocopolyheteronuclear aromatic moiety,

10 Z is carboxylate or trifluoroacetate, and

w is an integer greater than one and less than 200.

80. A method for producing a network of carbon fibrils comprising contacting carbon fibrils with a 15 strong oxidizing agent for a period of time sufficient to oxidize the surface of said carbon fibrils; contacting said surface-oxidized fibrils with reactant suitable for adding a functional group to the surface of the carbon fibrils; and further contacting said surface- 20 functionalized fibrils with an amount of a cross-linking agent effective for producing a network of carbon fibrils.

81. A method for producing a network of carbon fibrils comprising the steps of:

25 (a) contacting the fibrils with a solution of an alkali metal chlorate in a strong acid for a period of time sufficient to oxidize the surface of said fibrils;

30 (b) contacting the surface-oxidized fibrils with a reactant suitable for adding a functional group to the surface of the carbon fibrils; and

(c) further contacting said 35 functionalized fibrils with an effective amount of a cross-linking agent.

82. A method as recited in claims 81 or 82, wherein the cross-linking agent is a diol or diamine.

83. A method for producing a network of carbon fibrils comprising contacting carbon fibrils with a 5 strong oxidizing agent for a period of time sufficient to oxidize the surface of said carbon fibrils and contacting said surface-oxidized fibrils with an amount of a cross-linking agent effective for producing a network of carbon fibrils.

10 84. A method as recited in claim 83, wherein the strong oxidizing agent is an alkali metal chlorate or nitric acid.

85. A method as recited in claim 83, wherein the cross-linking agent is a polyol or polyamine.

15 86. A method for producing a network of functionalized fibrils comprising reacting at least two functionalized fibrils with a linker moiety comprising a bifunctional or polyfunctional moiety.

20 87. A surface-functionalized carbon fibril formed by the method comprising the steps of contacting carbon fibrils with an effective amount of a strong oxidizing agent for a period of time sufficient to oxidize the surface of said fibrils; and further contacting said fibrils with reactant suitable for adding 25 a functional group to the surface of said fibrils.

88. A surface-modified carbon fibril comprising a carbon fibril whose surface is uniformly substituted with a functional group.

30 89. A surface-modified carbon fibril as claimed in claim 88, wherein the functional group is carboxyl.

90. A method of uniformly substituting the surface of carbon fibrils with a functional group comprising contacting carbon fibrils with an effective 35 amount a of reactant capable of uniformly substituting a functional group onto the surface of said carbon fibrils.

91. A method of uniformly substituting the surface of carbon fibrils with a functional group as claimed in claim 90, wherein the functional group is carboxyl.

5 92. A method as recited in claim 90, wherein the reactant is a functionalized porphyrin.

93. A method as recited in claim 90, wherein the reactant is a phthalocyanine.

10 94. A method as recited in claim 93, wherein the phthalocyanine is cobalt phthalocyanine.

95. A surface-modified carbon fibril made by the method comprising contacting carbon fibrils with an effective amount of a reactant for substituting a functional group onto the surface of said carbon fibrils.

15 96. A surface-modified carbon fibril as recited in claim 95, wherein the reactant is a functionalized porphyrin.

97. A surface-modified carbon fibril as recited in claim 96, wherein the reactant is a 20 phthalocyanine.

98. A surface-modified carbon fibril as recited in claim 97, wherein the phthalocyanine is cobalt phthalocyanine..

99. A network of carbon fibrils formed by a 25 method comprising the steps of:

(a) contacting carbon fibrils with an oxidizing agent for a period of time sufficient to oxidize the surface of said fibrils;

30 (b) contacting the surface-oxidized fibrils with reactant suitable for adding a functional group to the surface of the fibrils; and

(c) further contacting said surface-functionalized fibrils with an effective amount of a cross-linking agent.

100. An electrode comprising functionalized nanotubes.

101. An electrode as recited in claim 100, wherein the functionalized nanotubes is phthalocyanine 5 substituted nanotubes.

102. A reinforced ceramic material comprising functionalized nanotubes dispersed in a ceramic matrix material.

103. A reinforced ceramic material produced by 10 dispersing a functionalized nanotube in an aqueous solution containing a hydrolyzable precursor of the ceramic material and converting the hydrolyzable precursor to a reinforced ceramic material.

104. A method of making a reinforced ceramic 15 material comprising dispersing a functionalized nanotube in an aqueous solution containing a hydrolyzable precursor of a ceramic matrix material and converting the hydrolyzable precursor to a reinforced ceramic material.

105. A sol gel material comprising the 20 functionalized nanotubes.

106. A porous material comprising a multiplicity of functionalized nanotube networks as defined in claims 78 or 79.

107. An adsorbent material comprising the 25 porous material of claim 103.

108. A catalyst support material comprising the porous material of claim 103.

109. A chromatography media material comprising the porous material of claim 103.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/16159

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :F16L 11/00; B01D 35/00; B05D 3/00; B29D 22/00
US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 138/137, 177, 178; 210/500.1, 500.23, 500.27; 427/399; 428/34.1, 408, 411.1

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A,P	US, A, 5,424,054 (BETHUNE et al) 13 June 1995, see entire document.	1-109
T	ZURER, P.S. Supramolecular Chemistry Exploited To Build Nanotubes, Recognize DNA. Chemical & Engineering News January 15, 1996, pages 18-22.	1-109

 Further documents are listed in the continuation of Box C. See patent family annex.

Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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	"&"	document member of the same patent family

Date of the actual completion of the international search

13 MAY 1996

Date of mailing of the international search report

16 MAY 1996

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INTERNATIONAL SEARCH REPORT

International application No.

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A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

138/137, 177, 178; 210/500.1, 500.23, 500.27; 427/399; 428/34.1, 408, 411.1



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